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NOVEL APPROACHES TO TRACE METAL SPECIATION

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Novel Approaches to Trace Metal Speciation

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Abstract

It is now generally recognised that the form of metal occurrence affects the toxicity, availability and transport mechanisms of different metals. One promising method for measuring trace metal speciation is to separate the various forms chromatographically and detect these by atomic spectroscopy. The suitability of the various atomic spectroscopic techniques is discussed and their coupling to both gas and liquid chromatography reviewed.

The development of atom cells for coupled gas chromatography - atomic absorption spectroscopy is described. Tetraalkyllead compounds provided a model system in the optimisation of the five atom cells by a variable step size simplex procedure. The effects of various parameters on analytical performance are discussed. In the most sensitive atom cells the effluent from the chromatograph was fed to a small hydrogen flame and the atoms from this flame were swept into a flame or electrothermally heated ceramic tube. The ceramic tube increased atomic residence times giving detection limits of 17 pg for tetramethyllead and tetraethyllead with the flame heated tube and 10 pg with the electrothermally heated tube. The flame heated tube was simpler to operate and more robust. The atom cells developed have also been used to speciate volatile organometallic compounds of As, Hg, Pb and Se.

Liquid chromatography is able to separate a much wider range of species. The speciation of four reducible forms of arsenic was used to demonstrate the coupling of liquid chromatography with atomic spectroscopy. After separation, volatile hydrides were formed in a miniature continuous flow hydride generator prior to detection by flame atomic absorption, flame atomic fluorescence and inductively coupled plasma emission spectroscopy. The detection limits obtained were competitive with others reported with the advantage of real time peak detection and an analysis time of only ten minutes.

A number of future applications for trace metal speciation are discussed.

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1. INTRODUCTION

1.1 THE NEED FOR SPECIATION

It is now generally recognised that the form of occurrence of trace elements is a primary factor controlling their behaviour and fate in the environment and that different chemical and physical species of trace elements have different toxicological properties (1). This recognition has given impetus to the determination of different physico-chemical species formed by an element, i.e. speciation, rather than simple total element concentration.

1.1.1 Toxicological Considerations

Among the most dangerous and thus widely studied metal pollutants is mercury (2 - 5). The discovery of Minamata disease in 1956 demonstrated the need for mercury speciation. The devastation of aquatic, animal and human populations in the Minamata Bay area during the period 1956 to 1968 was caused by ingestion of mercury discharged from a chemical plant (6), primarily by aquatic life and its subsequent passage along the food chain. Among the numerous mercury compounds known, the causative substance of Minamata disease was found to be dimethylmercury (7). Diethyl- and di-n-propylmercury were also found to be causative agents (7). Other toxic mercury compounds, e.g. diphenyl compounds and acetates, are found in medicaments, pesticides and antiseptics. With regard to acute toxicity there is very little difference between these compounds (8); however, large differences exist in their chronic toxicity, as witnessed by the fact that only the three alkyl mercury compounds cause Minamata

disease (7). Thus it is obvious that in this case total mercury or even total organic mercury values are of limited use to the toxicologist.

Such problems, however, are not confined to mercury since the fate and toxicity of many metals (1) are probably due to the molecular species in which the metal is bound rather than simply the metallic constituent alone. For example, tetraethyllead, TEL, which is used as an "antiknock" fuel additive, has toxicological properties quite different from those of inorganic lead salts, both as to the toxic dose and to the resultant biological effects (9). For inorganic lead salts, the intravenous LD_{50} in the rat is approximately 70 $mg.Kg^{-1}$ (10), whereas for TEL the figure is approximately 10 $mg.Kg^{-1}$ (11). The signs of poisoning are also quite different; a rat given TEL exhibits a high state of excitability, particularly to external stimuli, and generalized muscle tremors, whereas rats given inorganic lead salts experience only a transient loss of appetite and die without any manifestation of encephalopathy. The preceding statement intimates that TEL is the lethal agent. This is false, since TEL is susceptible to dealkylation in the liver and all evidence points to the dealkylated metabolite, triethyllead, as being the toxic agent (9). Tetramethyllead, TML, which is also used as a fuel additive, demonstrates similar toxic effects and, as for TEL, the toxic agent is thought to be the trimethyl metabolite.

1.1.2 Bioaccumulation and Methylation

The speciation of trace metals may have a profound effect on their bioavailability, for example vitamin B_{12} is the only assimilable chemical form of cobalt (12). Similarly change in oxidation state of metals greatly affects bioavailability and toxicity. Chromium (III) is an essential element, whereas chromium (VI) is highly toxic; indeed, most usable chromium is provided by a group of chromium amino acid complexes, the glucose tolerance factor (13).

The methylation of mercury by methanogenic microorganisms was discovered more than a decade ago (14) and there is now a considerable amount of detail on the subject (15). Whilst the mechanism of the methylation process is not fully understood, some detailed work has been carried out on the kinetics of the methylation process in aerobic and anaerobic media (16). The value of this type of study is that the rate data are very important to the design of quantitative models of heavy metal cycling in aquatic systems for effective water quality management. More recently it has been suggested that biological methylation is important in the formation of organometallic compounds of As, Pb, and Se, such as alkyl arsines (17, 18, 19), tetramethyllead (20, 21) and dimethylselenide (18, 22). Challenger (23) cited the "Forest of Dean" Case, in which the deaths of two children, in 1931, was attributed "to dysentry and exposure to arsenic generated in the house in a gaseous form." The arsenic compound was later found to be trimethylarsine, which was generated from arsenic pigments in the wallpaper by moulds growing on the paper. This and other cases led to much study of biological methylation (23

and references therein). Methylation of tin may also occur, being catalysed by a tin- and mercury-tolerant strain of Pseudomonas (24 - 27). There is considerable controversy as to whether the methylation of lead occurs (21, 28 - 30) or does not occur (31) and if it does, whether biological mechanisms need to be invoked (32, 33). The situation is further complicated by the fact that the compounds may be unstable in the conditions encountered in natural waters. For example, no tetraalkyllead compounds have been detected in river water or rain water samples, and when such compounds were added to river water rapid decomposition - 60% of the original amount after 24 hrs - took place (34). Thus the need for speciation coupled with sensitive detection is evident.

1.2 General Approaches to Speciation

An obvious way forward in the speciation of the various chemical or physical forms of a trace metal lies in the utilization of the separation power of established analytical separation techniques. In theory the separation of different metal species by one form of chromatography or another is possible. A number of practical difficulties arise, particularly when the separation is applied to real samples. To be of use a detection system able to identify the eluting species unequivocably and at sufficiently low concentrations is required. Additionally the metallic species should withstand the physical conditions of the separation process preferably so as to be eluted intact.

Gas chromatography (35 - 37), liquid chromatography (37, 38), and thin layer chromatography (37) have all been used for the separation of metal species in various chemical and physical environments. The latter technique is rarely used with flow-through detectors and will not be considered further.

1.2.1 Gas Chromatography

The separation of metal species by GC has followed two main pathways. Firstly, direct separation of organometallic species, which have sufficient volatility, e.g. organomercurials (36). Secondly, inorganic GC, where relatively involatile species may be separated after the preparation of volatile derivitives (35, 37).

1.2.1.1 Detectors for Metallic Species

The use of flame ionization detection, although universally popular for organic compounds, has certain limitations when applied to organometallic compounds. For example, in the detection of organotin compounds, drift in detector sensitivity has been noted (39), due to the build up of SnO_2 in the detector. This problem may be overcome; for instance, in the detection of TML and TEL in petrol (40, 41) flame ionization was used to detect the species as methane and ethane after catalytic hydrogenation. Despite the long linear range of this detector, it has proved unpopular for organometallic detection. This is probably due to the very universality which is the major advantage of the FID. It is difficult in real samples to identify unequivocably trace organometallic compounds amongst complicated organic matrices.

Electron capture detectors, ECDs, have proved popular, especially when the organometallic species contain a halogen atom. Sumino (42), in an exhaustive study of the chromatographic conditions required for the determination of organomercurials, was able to detect 1 pg of methylmercury chloride. The response of the ECD to organometallic compounds not containing a halogen whilst being greater than that to simple organic species, is much less than the response to halogen containing species. Thus, in the detection of dialkyl- and diaryl-mercury compounds (36 and refs therein), conversion to the halide salt prior to determination, increased the sensitivity of detection. The sensitivity of the ECD necessitates the careful clean up of all reagents and solvents to avoid interferences. Problems may also arise from the matrix; for example, the GC-ECD of tetraalkyllead compounds in petrol

(43 - 45), gave sensitive detection of lead. However, volatile halogen compounds, used as scavengers for lead in petrol, can cause problems in chromatographic interpretation unless steps are taken to remove them with scrubber columns.

For metal chelates, whilst FID has been used with detection limits of 0.1-1.0 ng, by far the most popular detector system has been electron capture (35). This is not altogether surprising, since many of the chelating ligands used are heavily fluorinated and are highly responsive to electron capture detection with detection limits around the 10^{-14} $g.s^{-1}$ level. However, a major problem is the requirement to remove the excess free ligand from the solution to be injected, since failure to do so may result in contamination of the detector.

Flame photometric detectors have also been used for the detection of suitable organometallic compounds. For tetraalkyllead compounds (46), the detector proved relatively insensitive to lead, linear range of 0.25-25 µg; however, it has proved to be a very sensitive detector for organotin compounds (47 - 51), using a hydrogen rich flame and monitoring the SnH band (610 nm). The tin emission is shifted to a broad band at 360-490 nm (48) if a silicate flame enclosure is used. The sensitivity of this type of detector is highly dependant on the flame conditions, the point of measurement in the flame and the spectral emission properties of the metals detected.

The combination of mass spectrometry with gas chromatography (52) provides one of the most powerful tools available in analytical chemistry. The use of GC-MS with the output at selected m/e values

allows a high degree of selectivity for a given metal species or ligand type with pico-gram detection limits equivalent to those obtained by ECD (35, 37). The power of GC-MS couplings is that complete characterization of species may be achieved. Sowinski and Suffet (53) used a triple detector system to detect the presence of various boron hydrides in the atmosphere. The FPD showed boron to be present, microcoulmetric response indicated the presence of reducible species, and the ECD indicated electron deficient species. This combined information indicated the presence of a boron hydride as opposed to some other saturated organo-boron compound; however for absolute confirmation, GC-MS was used. Another advantage of MS detection lies in its ability to identify whether a species has remained unaltered by the chromatographic procedure. Baughman et al. (54) in a study of alkyl- and aryl-mercury compounds by using GC-MS found that these compounds broke down under the chromatographic conditions used. Nielsen et al. (55) used GC-MS with isotopic dilution for the detection of TML and TEL in the atmosphere, using single ion monitoring. This gave the advantage that compensation for any degradation of TML or TEL during sampling, storage or analysis could be made. The major problem with GC-MS systems is their great expense when compared with other GC detectors. As a result it is often preferable to use multi-detection systems to aid chromatographic interpretation.

For trace organometallic speciation, one of the problems with conventional detectors is that they do not respond solely to the metal of interest. The universal response of the FID makes identification of the organometallic species difficult. The enhanced response of the ECD to halogen-containing species means that for sensitive detection,

it is preferable to label the metal species with a halogen. This involves extensive sample work up and also may give a false representation of the distribution of trace organometallic species in the original sample. The flame photometric detector, whilst sensitive for some metals, lacks the ability to respond to a wide range of metallic species.

Thus, ideally what is required is a detector system which responds selectively to the metal in the organometallic species to give unequivocable identification at trace levels without extensive sample manipulation. The various atomic spectroscopic techniques are ideally suited to act as such detection systems. The various atomic absorption and atomic emission techniques have been widely used as detectors for total metal concentrations and coupling them with chromatography should enable speciation of trace organometallic species.

1.2.2 Liquid Chromatography

The separation of metallic species as simple cations, metal chelates and organometallic compounds has been reviewed by various authors (37, 38). Besides being able to separate involatile species not amenable to GC analysis, liquid chromatography may be used to separate volatile metals species which have low thermal stability and which therefore are not suitable to GC separation.

1.2.2.1 Detectors for Metallic Species

The speciation of metals may be achieved using conventional ultraviolet (UV) or molecular fluorescence detectors, either by complexation prior to separation (38), or by post column reaction, e.g. the complexation of organomercurials with dithizone prior to UV detection by Gast and Kraak (56). Obviously, by suitable choice of the chromophore or fluorophore for either post- or pre-column reaction, sensitive detection is possible, e.g. 60 ppb for phenylmercury compounds (56) using dithizone with UV (480 nm) detection.

For systems which have different metal species which react with the complexing agent, then a certain amount of ambiguity in chromatographic interpretation will result. This ambiguity may be resolved by using detectors which respond directly to the metal and not to the molecule, e.g. by using atomic spectroscopy.

Some organometallic compounds do not require such post- or pre-column reaction to be detected by conventional LC detectors. For example, Ruo et al. (57) used UV (254 nm) detection of tetraalkyllead compounds in gasoline, whilst at 254 nm the tetraalkyllead compounds absorb, saturated hydrocarbons do not; however, some olefins also absorb at this wavelength and therefore represent a possible interferent. The use of atomic absorption detection for tetraalkyllead compounds in gasoline, e.g. Botre et al. (58), enables specific detection of the organo-lead species with more than adequate sensitivity. Detection is a problem for non-absorbing species, e.g. short chain alkyltin compounds since they have virtually no absorption in the

near UV and also give low refractive index response (39). Burns and co-workers (59) found direct FAAS of HPLC effluents to be more sensitive than current spectrometric or fluorimetric method for alkyltin species.

Detectors for LC should not be viewed as mutually exclusive since they all yield potentially valuable information. For example, electrochemical detectors enable the detection of compounds which may be readily oxidized or reduced; similarly, atomic spectroscopy offers a unique approach to information about which metallic species are present in a system. A review of the coupling of LC with the various atomic spectroscopic techniques is given in Chapter 3 of this thesis.

2 A Review of Coupled Gas Chromatography - Atomic Spectroscopy Techniques

2.1 Introduction

Atomic spectroscopy offers the possibility to selectively detect a wide range of metals and non-metals. The use of detectors responsive only to selected elements in a multicomponent mixture drastically reduces the constraints placed on the chromatography, since only those components in the mixture which contain the element of interest will be detected. Thus, chromatographic separation is only necessary between components which contain the element of interest.

Certain requirements for such element specific detectors may be identified, these being good interelement selectivity, sensitive detection for a wide range of elements, simplicity of design and operation, and compatibility with existing instrumentation. These aspects are discussed further below.

2.1.1 Interelement Selectivity

Atomic absorption spectroscopy (AAS) is inherently the most selective of the atomic spectroscopic techniques due to the "lock and key" mechanism (see section 2.2.2). The various plasma emission sources: microwave induced plasma (MIP), direct current plasma (DCP), and inductively coupled plasma (ICP), due to their very high excitation temperatures, produce a wealth of emission lines. Thus, whilst not possessing the inherent selectivity of AAS, the use of a suitably high

resolution monochromator reduces the possibility of spectral interference and enables interelement selectivity. This wealth of emission lines produced also enables multi-element detection which normal line source AAS does not offer. Atomic fluorescence spectroscopy (AFS), using line source excitation, in theory offers similar selectivity to AAS, coupled with the multielement capacity of AES, but in practice is limited by the availability of suitable line sources.

2.1.2 Sensitive Detection

The availability of a sensitive detection system precludes excessive sample manipulation and preconcentration which is not only time consuming, but may cause sample contamination.

The most popular ways of generating atoms for AAS are in flames and by electrothermally heated furnaces. The former usually gives poorer detectability due to the shorter atomic residence times in the flame and problems of sample introduction. Relatively short useful linear ranges of 1-2 orders of magnitude are typical of absorption techniques. The plasma emission techniques use high temperature excitation sources, thus enabling low level detection of metals and the favourable source geometry often provides long linear working ranges. In atomic fluorescence, provided a suitably intense line source is available, then low level detection and long linear ranges are available.

2.1.3 Design, Operation and Compatability

Flames or plasmas, whether chemical, in FAAS and FAFS, or electrical, in the ICP, DCP and MIP, being made up of flowing gas streams, are well suited to accept an analyte in a gas stream. Their continuous mode of operation is also advantageous, since although the analyte peak is transient, it is introduced in a flowing gas stream. Electrothermal atomizers are typically not continuous in their mode of operation and are designed for use with discrete condensed phase samples and thus require modification before they may accept a flowing gas stream.

The usefulness of the various atomic spectroscopic techniques as detectors for GC and their applications will now be reviewed.

2.2 CHOICE OF SPECTROSCOPIC TECHNIQUE

2.2.1 Atomic Emission Spectrometry

The probability of transitions between given energy levels of a fixed atomic population was expressed by Einstein in three transition probabilities: A_{ji}, B_{ij} and B_{ji}, which refer to spontaneous emission, absorption and stimulated emission respectively. They may be considered as representing the ratio of the number of atoms undergoing transition to the number in an initial level. The intensity, I_{em}, of a spontaneous emission line is related to A_{ji} by the equation

$$I_{em} = A_{ji} h\nu_{ji} N_j \qquad \ldots (2.1)$$

When a system is in thermodynamic equilibrium, the number of atoms, N_j, in the excited state is given by the Boltzmann distribution law:

$$N_j = \frac{N_o g_j}{g_o} \exp\left[-(E_j/kT)\right] \qquad \ldots (2.2)$$

where N_o is the number of atoms in the ground state with an energy E_o, g_o and g_j are the statistical weights of the ground and jth states respectively, where $g = 2J + 1$, and k is a constant.

$$\frac{N_j}{N_o} = \frac{g_j \exp\left[-(E_j/kT)\right]}{g_o \exp\left[-(E_o/kT)\right]} \qquad \ldots (2.3)$$

The total number of atoms present, N, will be the sum of the atoms occupying all the energy levels i.e. $N = \Sigma_j N_j$

$$\frac{N_j}{N} = \frac{g_j \exp\left[-(E_j/kT)\right]}{\Sigma_j g_j \exp\left[-(E_j/kT)\right]}$$

$$= \frac{g_j \exp\left[-(E_j/kT)\right]}{F(T)} \qquad \ldots (2.4)$$

where F(T) is the partition function. If self absorption is neglected for a system in thermodynamic equilibrium, then:

$$I_{em} = A_{ji} h\nu_{ji} N g_j \exp\left[-(E_j/kT)\right] \quad /F(T) \qquad \ldots (2.5)$$

Thus, if the analyte atom concentration is small, i.e. self absorption is negligible, then I_{em} is directly related to emission intensity. The emission intensity is also critically dependant of the emission source temperature and small fluctuations in this temperature cause large changes in I_{em}. With "hot" emission sources, e.g. plasmas, a wide choice of sensitive analytical lines will be available. This is both an advantage and a disadvantage. The wealth of lines of varying sensitivity enables a wide range of analyte concentrations to be dealt with; however, the possibility of spectral interference from line overlap requires high resolution, and hence high cost, optics.

The various plasma emission techniques - microwave induced, direct current and inductively coupled -, with their high excitation temperatures, have all been used as detectors for gas chromatography (60, 61), and far more reports refer to these sources than to any other emission source. Of the three plasma sources, the microwave plasma have proved the most popular.

2.2.1.1 Microwave Induced Plasma Emission Spectroscopy

The microwave induced plasma, MIP, derives its power from a high frequency, 2450 MHz, magnetron valve which is coupled via a waveguide and resonance cavity into the plasma gas. The plasma is normally sustained in a small bore, approximately 2 mm. i.d., quartz tube, with argon or helium flowing through. Stable argon plasmas with conventional cavities may be achieved at both reduced and atmospheric pressure. For helium stable plasmas are only achieved with conventional cavities with pressures below 65 mbar (62). Atmospheric pressure helium plasmas may be sustained if the TM_{010} (Beenakker) cavity (63, 64) is used. The temperature of the plasma is difficult to define as it is not in local thermal equilibrium, LTE, as evidenced by the low neutral gas temperature of <1000 K compared to the excitation temperature of 4500 K to 5500 K (65). The presence of high energy electrons and metastable excited inert gas species make the plasma an extremely efficient excitation source. The energy of the lowest metastable state (66) of atomic helium, neutral and ionized diatomic helium and atomic argon (19.73, 13.3 - 15.9, 18.3 - 20.5 and 11.5 eV respectively) not only shows the source to be highly energetic, but explains the fact that some elements do not give characteristic line emission in argon but do so in helium. The MIP allows atomic lines of some non-metals, e.g.

chlorine, to be monitored.

The low gas temperature of the MIP reduces the amount of sample it can withstand without being extinguished. Thus coupling the MIP with GC where the amounts of solute are small and the carrier gas is the same as the plasma gas provides a favourable sample introduction method. This is reinforced by the number of reported couplings of GC to MIP - see Table 1.

In 1965 McCormack et al. (67) first used the MIP as an element selective detector for organic compounds. The effluent from the GC was taken directly to the silica tube containing the plasma discharge. Both tapered and coaxial cavities were used, the former being more sensitive, whilst the latter would accept larger samples. Two plasma types were utilized: low pressure helium and atmospheric argon; the latter was favoured because of the complexity of the associated vacuum system required with the former. The atmospheric argon plasma was then used by Bache and Lisk for the determination of pesticides in various samples by element selective detection of phosphorus (68) and iodine (69). The same authors also used a low pressure argon plasma for phosphorus selective detection in pesticides (70), with a decrease in detection limit of an order of magnitude over the atmospheric pressure plasma (68). The more energetic reduced pressure helium plasma was used for the determination of halogens, phosphorus and sulphur using atomic lines (71 - 73). Moye (74) preferred the tapered rectangular cavity to the Evenson $\frac{1}{4}$ wave cavity and used a mixed argon/helium, 15 + 85, carrier which gave a lower background emission for chlorine, iodine and phosphorus detection in pesticide residues.

Dagnall et al. (62, 75) used a quarter wave radial cavity for low pressure argon or helium plasmas in the determination of sulphur in various compounds. It was found that the most sensitive and specific emission wavelength was not the same for all the compounds examined. In addition thioglycolic acid was found to be very difficult to fragment (62) and a platinum wire in the base of the detector was found to catalyse the fragmentation process (75). Bach and Lisk (76) were the first to use the low pressure helium plasma for detection of organomercury compounds after extracting the compounds from salmon using the established procedures of Westöö (14, 77, 78). Dagnall et al. (79) signalled a potential use of the MIP detector for obtaining interelement ratios by using two monochromators, one set at a carbon line and the other set to monitor a heteroatom. Other workers (80 - 84) have also used the MIP detector to determine inter-element ratios in an attempt to estimate empirical formulae. The commercially available MPD850 (Applied Chromatography Systems) low pressure helium plasma system has been used in this role (81 - 83). Dingjan and De Jong (84) found a reference compound was required if accurate ratio formulae were to be obtained. Schwarz et al. (85) used an oscillating slit mechanism for the determination of hydrogen isotope ratios but the poor signal to noise ratios obtained resulted in poor precisions.

The passage of carbon containing compounds through the plasma may cause carbon deposits to be formed on the walls of the quartz capillary, absorbing part of the radiation and increasing background emission (67). This can be prevented by either initiating the plasma after the solvent has passed through the detector (68), or by adding traces of a scavenging gas. This gas may be either nitrogen (80),

oxygen (80, 86) or air (67) added to the plasma gas; however as a result the spectral background is considerably increased. The MIP has proved popular as a detector for various metal chelates (86 - 88, 90, 91), and also as a detector for various hydride forming elements (92 - 96). Talami and Bostick (92) determined alkylarsenical acid compounds in pesticides by generating their hydrides prior to GC-MIP analysis. The separation and sequential detection of As, Ge, Se, Sn, and Sb hydrides (93 - 96) has been demonstrated using a mixed argon/helium plasma (93, 95, 96). Mulligan et al. (94) evaluated various cavities for microwave plasmas and found little difference in detection power achieved, but found the Beenakker TM_{010} cavity easiest to operate. The method was used to determine the above hydride forming elements in whole blood and enriched flour (95) and NBS orchard leaves (95, 96).

The GC-MIP couplings have also been used for the detection of various metals in volatile organometallic compounds. Lead has been determined as the tetraalkyl species (97 - 100), in petrol (99, 100), in the atmosphere (98), and as trialkylleadchloride in water samples (101). Mercury as the diphenyl (97), dimethyl and diethyl (102) derivatives have been detected using the TM_{010} cavity. Quimby et al. (97) used the same cavity to determine manganese as the methylcyclopentadienyltricarbonyl derivative in petrol and as a silicon specific detector for tetravinylsilane. The group at Amherst have demonstrated the couplings of capillary columns with the TM_{010} cavity (99, 101, 103 - 105) with great success for metal specific detection of volatile organometallics. In their study of the pyrolysis of carborane silicone polymers (105) it was found that doping of the

plasma gas with hydrogen inhibited oxide or silicate formation by promoting borohydride formation, which increased the population of atomic boron rather than ionic states. Hanie et al. (106) have also used capillary columns for the determination of halides in pesticides using a helium plasma and a surfatron cavity (107). Thus it may be seen that microwave plasmas have been used widely for element selective detection with the possibility of further applications yet to be reported. The above and other work in couple GC-MIP systems are summarized in Table I.

Table I. Coupled Gas Chromatography - Microwave Induced Plasma Optical Emission Spectroscopy

Detector	Chromatography	Matrix	Sample treatment/comments	Element	Wavelength (nm)	Detection Limit	Reference
Tapered and coaxial cavities used, the former more sensitive, the latter accepted larger samples. 10 mm. i.d. discharge tube at low pressure.		Solutions of simple and heteroatom containing organic compounds.	At low pressure He was the preferred carrier gas. At atmos. pressure Ar was used since it gave a stable discharge. Dynamic range 4 orders of magnitude.	C	388.3	2×10^{-16}	
				F	516.6	3×10^{-14}	
					251.6	3×10^{-12}	
				Cl	278.8	5×10^{-10}	
				Br	298.5	8×10^{-10}	
				I	206.2	2×10^{-7}	
				S	257.5	7×10^{-14}	
						1×10^{-9} g/sec.	67
Atmos. pressure Ar 1 mm. i.d. quartz discharge	2' glass 'U' column, 5 mm. i.d. 5% SE 30	Organophosphorus insecticide	Diazinon Dimethoate, Ethion Parathion	P	253.565	1.4 to 9.2 $pg \cdot s^{-1}$	68 contd

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
tube in a tapered cavity.	on 80/100 Chromosorb W T_c = 160-200 Ar = 20-115 ml/min used.	residues in pure form, agricultural + food samples.	and Ronnel determined.				68
As in ref. 68	See ref. 68	Iodinated herbicide residues and metabolites in wheat, oats and soil.	Detection of Ionynil and metabolites Recoveries from 66-108% achieved.	I I_2 band	206.2	4×10^{-10} $gI_2\ s^{-1}$	69
As in ref. 68 Except reduced pressure Ar plasma.	See ref. 68	Diazinon in grapes; see ref. 68	See ref. 68 achieved increased sensitivity with low pressure discharge.	P	253.565	6×10^{-13} $g\ s^{-1}$ of P	70

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Reduced pressure helium plasma using tapered cavity. 5-10 mm. Hg pressure.	6' glass column 10% DC-200 on 80/100 mesh Gas Chrom Q, Isothermal at various T_c = 130°C to 210°C	Organic compounds and pesticides		Br	478.55	2×10^{-11} g s^{-1}	71
				Cl	479.45	6×10^{-11} g s^{-1}	
				I	533.82	5×10^{-11} g s^{-1}	
				P	253.57	9×10^{-12} g s^{-1}	
				S	545.38	5×10^{-11} g s^{-1}	
Ar/He (15 + 85) mixed plasma, tapered cavity as longer lifetimes and less background emission obtained.	4' x 1/8"i.d.glass glass, 5% SE 30 on Gas Chrom. Q T_c = 180°C, T_I = 215°C Flow rate = 27 ml min^{-1}	Pesticide residues of various P, Cl and I containing compounds		P	253.57	.07 ng	74
				Cl	221.00	11.5 ng	
				I	206.20	0.5 ng	
Reduced pressure helium plasma	6' x 1/8"i.d. glass, 10% DC -200 on 100/	Phenol substituted insecticides in	Monitored atomic S and Cl lines	Cl	479.45		72 contd
				S	545.38		

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	120 mesh gas Chrom. Q.	agricultural samples.					72
¼ λ radial line cavity, Ar or He low press. (13–40 mbar) plasma.	2.7 m. x 6.5 mm. i.d. Cu tubing packed with dinonyl phthalate 1.0 µl injections.	S compounds CS_2 thiophene, thioglycolic acid, DMSO, SO_2.	Thioglycollic and difficult to fragment.	S	S - 190.0 S - 191.5 C=S- 257.6. C_2- 516 common to all compounds.	0.2 ng for CS_2 at C=S band-head.	62
See ref. 62.	0.6 mm. x 6mm. i.d. Cu tubing packed with either Porapack P or Q.	S compounds CS_2, thiophene, dimethylsulphide and thioglycolic acid.	Used Pt wire in base of detector to catalyse fragmentation process.	S C	Monitored C=S band-head at 257.6 and atomic C line at 247.9.	Low ng range	75

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Low pressure (5-10 T) He plasma See ref. 70.	See ref. 70.	S, halogen and P containing pesticide residues in a wide range of food products.		Br, Cl, I, S, P.	See ref. 71		73
Reduced pressure He plasma in a tapered cavity cf. ref. 71.	2' x 5/32" i.d. glass column, 60/80 mesh Chromosorb 101 T_c = 100°C T_I = 140°C He = 80 cm^3/min.	Me_2Hg	Westöö estraction procedure, (14, 77, 78) for MeHgCl in salmon. Linear range: 0.1-100 ng for MgHgCl.	Hg	253.7		76 contd.

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	6' x 5/32" i.d. glass column, 20% OV17 and QF1 (1+1 w/w) on 80/100 mesh, Gas Chrom Q, T_I = 208°C, T_c = 152°C	Methylmercury dicyandiamide, Phenylmercuric acetate, methylmercury dithizonate, MeHgCl in salmon.					76
Atmospheric Ar plasma, 20 cm x 2 mm. i.d. quartz tube surrounded by ¾ λ cavity.	30 and 70 cm x 6 mm. i.d. packed with Porapak S.	Range of C, O, N, and halogen containing compounds.	Several cavities examined, ¾ λ preferred because it produced a long (ca. 8 cm.) stable discharge with little local overheating.	C	Monitored, atomic C line at 247.9, C_2 bandhead at 516.5 and C_2/CN bandhead at 385-9	10 → 20 pg.s^{-1}	111

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
See ref. 111.	0.7 m x 1/8" stainless steel, Chromosorb 101.	Range of C, S, and halogen containing compounds.	Use of 2 monochromators - 1 set to atomic C line, other set to heteroatom line. By monitoring emission from both obtain interelement ratios.	C	247.9	.19 ng.s^{-1}	
				I	206.2	.1 "	
				S	182.0	.04 "	
				P	253.5	.3 "	
				Cl	256 (band)	4.5 "	
				Br	292 (band)	2.5 "	79
Ar plasma. Essentially the same as 67.	10' x ¼" i.d. stainless steel column, 20% Carbowax 20 M on Chromosorb P 60/80 mesh,	Me_2Hg	Found selectivity for Hg over various organic compounds, always $\geq 10^3$	Hg	253.7	0.3 ng	108 contd.

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	Ar = 48 $cm^3 min^{-1}$						
	T_c = 75°C						108
Low pressure He plasma using MPD 850 system, O_2 and N_2 used as scavengers to prevent C build-up.		Various organic compounds.		C	247.8	.08 $ng.s^{-1}$	
				H	486.1	.03 "	
				D	656.2	.09 "	
				O	777.2	3.0 "	
				N	746.9	2.9 "	
				F	685.6	.06 "	
				Cl	479.4	.06 "	
				Br	470.5	.12 "	
				I	516.1	.05 "	
				S	545.4	.09 "	109

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Similar system to 111, except ¼ λ Evenson cavity 70W forward power Ar plasma, ignited after elution of solvent.	2 columns, both 0.6 m x 4.8 mm i.d., 1. Universal B coated with 10% Apiezon L. 2. 0.5% Apiezon L on glass beads (0.2 mm. diam.) Both conditioned for 36 hrs at 200°C.	acac and tfa chelates of Al, Cr, Cu, Ga, Fe, Sc, V.	MIP responded both nonspecifically to C or specifically to the metal of interest.	Al Cr Cu Ga Fe Sc V	396.2 357.9 324.7 294.4 344.1 361.4 318.4	in the range 2×10^{-12} to 2×10^{-11} $g.s^{-1}$	87
¼ λ Evenson cavity used, reduced pressure (10T)	1 cm or 2 cm x 1 mm i.d. Cu tubing packed	CO, CO_2, SO_2, N_2O in air.	Gas mixtures were prepared by injecting	C N S	247.9 337.1 (N_2 bandhead) 190.0	CO 50 ppm CO_2 50 " N_2O 20 "	110 contd.

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
He plasma generated in a 6 cm x 8 mm i.d. quartz tube.	with either Porapak Q or 5A molecular sieve T_c = 125°C 50 l injections		known amounts of pure gas into an air filled flask fitted with a septum.			SO_2 30 ppm	110
Ar plasma generated in a quartz papillary 1.6 mm i.d. x 25 cm placed in a tapepered rectangular type cavity.	Stainless steel tubing 72 cm x 4 mm. i.d., 0.5% SE-30 on glass beads 60/80 mesh. T_c = 160°C. T_I = 200-210°C Ar = 150 $cm^3 min^{-1}$.	Metal acac chelates desolved in chloroform.	A CN band was observed for all complexes probably due to N_2 impurity in the Ar. Failed to chromatograph acac chelates of Cu (II), Fe (III) and V(IV).	Al Be Cr	396.2 234.9 425.4	Al=100 ng Be=0.01ng Cr=0.1ng	88

contd.

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
			2 orders of magnitude for Be and Cr. 1 order for Al.				88
Reduced pressure He plasma, 0.1-1%. O_2 or N_2 added as scavenger.	3 m x 2.5 mm. i.d., 10% Apiezon L on 60/80 mesh DCMS treated Chromosorb W Effluent split 1:1 to FID and MIP.	Wide range of organic solutions.	Multi-nonmetallic element detection used to calculate empirical formula of organic compounds. Linear range: 4 orders of magnitude for F.	C	See 109.	C=0.08ngs^{-1}	
				H		H=0.03 "	
				D		D=0.09 "	
				F		F=0.06 "	
				Cl		Cl=0.06 "	
				Br		Br=0.09 "	
				I		I=0.05 "	
				S		S=0.09 "	
				N		N=2.9 "	
				O		O=3.0 "	80

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Reduced pressure He plasma doped with 1% O_2, ¼λ Evenson cavity.	'U' tube columns packed with Chromosorb W-HP with 3% OV-101 loading.	Chelates $Cr(tfa)_3$, $Cr(acac)_3$, $Cr(hfa)_3$.	Use of MPD as a specific detector for Cr; and as a non-specific detector, by monitoring the atomic C line.	Cr	357.87	1.5×10^{-11} to 8.0×10^{-10} gs^{-1} of Cr.	86
Tapered cavity system essentially the same as 67. Ar plasma, 35W forward power.	4' x 0.5 mm. i.d. glass column packed with 4% SE-30 on 30/60 mesh Chromosorb GHP.	Se cpds in environmental samples, looked at various NBS materials, with good agreement.	Se(IV) complexed with PD to form the volatile piaselenol complex followed by toluene extraction.	Se	204	40 pg Se $0.1\ \mu g l^{-1}$ for water samples and 15 ppb for solid samples.	112

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Ar plasma (see 112.) atmospheric pressure.	3' column, 4% FFAP on 80/100 mesh Gas Chrom Q. Ar = 90 cm^3 min^{-1}. T_c = 150°C. T_I = 200°C.	MeHgX in benzene extracts of biological samples, and air.	X designates Cl, Br, I or OH since all eluted simultaneously; see 129, 130 for explanation of this.	Hg	253.7	CH_3 HgCl = 0.5 pg $(CH_3)_2Hg$ = 2 pg in water = 1 $ng.l^{-1}$ in fish 1 $ng.g^{-1}$	
	3' column, 1% FFAP on 80/100 mesh carbon beads. Ar = 95 cm^3min^{-1} T_c = 135°C T_I = 200°C	CH_3HgX in water and air					
Reduced pressure 1 - 10 T , He	2' column, Chromosorb 101	$(CH_3)_2Hg$ in water and air					113 contd

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
plasma.	He = 80 $cm^3 min^{-1}$.						
	T_c = 115°C.						
	T_I = 135°C.						113
Atmospheric pressure Ar plasma, 30W forward power, see 112.	3' column, 4% FFAP on 80/100 mesh. Gas Chrom Q.	As and Sb in environmental samples.	As(III) and Sb(III) converted to Ph_3AsH and Ph_3SbH, extracted into ether, separated by GC.	As Sb	228.8 259.8	20 pg. 50 pg.	
	Ar = 110-120 cm^3 $-min^{-1}$.						
	T_c = 220-240°C.						
	T_I = 245-260°C.						114

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
See 112.	6' column, 5% Carbowax 20 M on 80/100 mesh Chromosorb 101 T_c = 175°C. T_I = 180°C. Ar = 100 cm^3-min^{-1}.	Alkylarsenic acids in pesticide and environmental samples, MMA and DMA.	As cpds converted to hydrides. Detailed study of hydride generation and trappingsof the evolved arsines. Linear range 0.01-20 ppm.	As	228.8	20 pg as As 0.25 $\mu g.l^{-1}$ in water samples.	92
¼λ Evenson cavity. Atmospheric pressure. Ar plasma, 70W forward power.	0.9 m teflon column 3 mm.id. 10%SE30 on 70/80 mesh Gas Chrom Z.	Human blood serum.	Low temp. ashing followed by chelation with H(tfa) to form $Cr(tfa)_3$ which	Cr	357.9	9 x 10^{-13} g Cr.	90 contd

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	T_c = 180-190 T_I = 200 Ar=30-150 ml min^{-1}		is extracted into benzene. Linear range 1 - 10 pg Cr.				90
Low pressure (150 mbar) He plasma cavity type 214L Interelement selectivity improved by use of wavelength modulation.		Organic compounds Hg(Me)Cl.	Demonstrated that at low pressures fragmentation occurs via collisions with atomic He whereas at high pressures the collisions are with He_2. Linear range 0.02-0.5 ng.	Hg	253.65	5×10^{-14} g	115

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Atmospheric pressure Ar plasma in quartz capillary 1.6 mm i.d. x 25 cm. Tapered rectangular cavity, 50W forward power.	Column - 45 cm x 3 mm i.d. glass, 0.5% SE30 on 60/80 mesh glass beads. T_c = 140°C. T_I = 180°C. Ar = 80 cm^3 $-min^{-1}$.	Trace levels of Cu and Al in Zn metal.	Cu and Al extracted as tfa chelates in CCl_4. Linear up to 60ng Cu, 100ng Al.	Cu Al	324.8 396.2	1 ng 0.5 ng	91
See 112, 113. Ar plasma, 5-10T pres. 18W forward power	3' x 5 mm. i.d. glass, 6% FFAP on 80/100 mesh. Gas Chrom Q. T_c = 180-190°C T_I = 200°C Ar = 130-150 cm^3 min^{-1}	MeHgCl in water samples.	MeHgCl extracted as quaternary amine adducts	Hg	253.7	1-2.5 $ng.l^{-1}$ for water samples.	116

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Atmospheric pressure, He plasma using TM_{010} cavity.	Used exponential diluter to demonstrate the applicability of MIP for GC detection.	Gas mixtures	Demonstrates advantages of atmospheric pressure He plasma and discusses excitation mechanism. 3-4 orders of magnitude linear ranges.	C	193.1	2×10^{-11}	
					247.9	2×10^{-11}	
				H	486.1	2×10^{-9}	
				Cl	479.5	2×10^{-10}	
					481.0	3×10^{-10}	
				Br	470.5	6×10^{-11}	
					478.5	1×10^{-10}	
				I	516.1	2×10^{-11}	
					206.2	3×10^{-11}	
				S	545.4	8×10^{-10}	
						$mol.l^{-1}$.	64

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Low pressure (3-5T), Ar plasma; see 112, 113.	Glass column, 6' x 3.5 mm., 4% OV-101 on Chromosorb G (HP) 80/100 mesh. Ar = 80 ml min^{-1}	Mixture of n-paraffins and TMS- derivatives of carboxylic acids.	Duel FID/MPD (5:1 split) to demonstrate specificity of response to TMS derivatives. Linear range 0.5-150 ng.	Si	251.6		117
Low pressure (90T) He plasma, observation 8-9 mm downstream from centre of discharge, 75W forward power. 0.25% v/v O_2	Constant sample introduction for optimization studies.	Various organic compounds	Optimized plasma conditions for: gas flow rates observation position, microwave power, and gas pressure	Br C Cl F H I N O	470.47 247.86 479.45 685.6 486.13 516.12 746.88 777.19	0.01ng s^{-1} to 0.5ng s^{-1}	118 contd

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
as scavenger. or 0.4% v/v N_2 ¼λ Evenson cavity model 214L and ¼λ coaxial cavity model 217L.			with the 217L cavity up to 10% of power reflected, with 214L only 1% reflected. 3-4 decades except for H where a non-linear response is found.	S	545.39		118
See ref. 109 Reduced pressure He plasma.		Various organic compounds.	Signals for four elements are monitored simultaneously	C,H,D,O, N,F,Cl,Br, I,S.	See 109		81 contd

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
			added by a SYNC signal, stored for latter computer analysis, resulting in interelement ratios; main concern is in data acquisition and processing.				81
See ref. 109 Reduced pressure He plasma.	None given.	Trace S in MeOH, yellow P in PCl_3 specific detection	Used MPD 850 to obtain accurate empirical formulae,	C,H,D,O, F,Cl,Br, I,P,S.	See 109.		82 contd

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
		of vinylidene and PCB's.	obtain detection limits comparable to manufacturers' claims.				82
Mixed Ar/He plasma, 110W forward power 0W reflected.	Polypenco nylaflow pressure tubing 4.7 mm. i.d., 1', 3', and 6' lengths. Packed with Chromosorb 102 60/80 mesh.	Hydrides generated from solutions of As,Ge,Sb,Se and Sn.	Hydride trapped in liq. N_2 then chromatographed Elements determined sequentially. Linear over 2 orders of magnitude.	Ge As Se Sn Sb	303.9 193.7 196.0 317.5 259.8	3 ng 7 ng 25 ng 40 ng 10 ng	93

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Atmospheric He plasma, TM_{010} cavity, 75-80W, forward power, axial viewing.	3'x 1/8", 5% OV 17 on 100/120 mesh Chromosorb 750 He = 70 cm^3 $-min^{-1}$.	Diphenyl mercury.	A design for heating the interface between GC and plasma utilizing nichrome resistance wire coupled to a variace given.	Hg	253.7	1.0pg s^{-1}	
	3'x 1/8", 3% QF-1 on 100/120 mesh.	TBP		P	253.6	2.1 "	
	Varaport 30 He = 50 cm^3min^{-1}	Tetravinyl-silane.		Si	251.6	29 "	
	6'x 1/8", 6% Carbowax 20M on 100/120 mesh Chromosorb P; He = 50 cm^3min^{-1}	MMT		Mn	257.6	0.25 "	97
	6'x 1/8" 2.5%						contd

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref
	Dexsil 300 on	TEL		Pb	283.3	0.49 pg s^{-1}	
	100/120 mesh	2-5 dimethyl-		S	545.4	63 "	
	Chromosorb 750	thiophene.		Cl	481.0	16 "	
	He = 50 $cm^3 min^{-1}$	Halobenzenes.		Br	470.5	10 "	
				F	685.6	8.5 "	
				I	206.2	31 "	97
¾ λ cylindrical	1.8m x 3.1 mm,	Tetraalkyllead	Samples cold	Pb	405.78	TML=6pg	
cavity, 125W for-	3% OV-1 on 80/-	compounds in	trapped on			TMEL=10 "	
ward power Ar	100 mesh Chro-	the atmosphere.	SE50 on Chromo-			DMDEL=23 "	
plasma, back-	mosorb W.		sorb P at -80°C.			MTEL=35 "	
ground correc-	Ar = 22 $cm^3 min^{-1}$		Removed by			TEL=40 "	
tion by wave-	T_c = 80°C		freeze drying				
length modula-	T_I = 130°C		and concentrated				
tion.			in organic				
			solvent.				98

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Low pressure (5T) He and Ar plasmas tapered rectangular cavity, 100W forward power. 0.3% O_2 added to plasma gas.	Stainless steel, 3m x 3mm i.d., 3% w/w Dexsil 300 on 80/100 mesh Chromosorb W(AW) 6m x 3mm i.d. Squalane on 80/100 mesh Chromosorb W(AW).	H in organic cpds.	He plasma twice as sensitive as Ar plasma due to higher energy and therefore more complete fragmentation.	H	656.28	10^{-11} g s^{-1}	121
See ref. 121.	See ref. 121.	H isotope ratios in organic cpds in water samples.	OSM measures alternately ^1H and ^2H emissions of hydrocarbons major disadvantage	^1H ^2H	656.28 656.10		85 contd

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
			is high S/N ratios.				85
Reduced pressure He plasma. See ref. 109.		PCBs in seal blubber, cleaning fluids in water.	Applications of MPD850 in analysis and also empirical formula.determinations.	C,H,O,N, F,Cl,Br, I,P,Se,As, Hg,Pb.		50 pg s^{-1} range	83
See ref. 109.		Biological tissues, coal tars, pesticides.	Brief resumé of the possible uses of the MPD850 system.	Cl,Br,I, S,P,Hg.			89

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Beenakker, $\frac{3}{4}\lambda$ Evenson, $\frac{1}{4}\lambda$ Broida, $\frac{1}{2}\lambda$ cavities were compared with He/Ar or Ar plasmas 100W forward power.	2.5" x 4.7 mm. Packed with Chromosorb 102, Served only to reduce rate of sample through-put to give stable plasma.	Standard solutions.	Semi-automated hydride generation from stock solution containing As, Ge, Sb, Sn. Beenakker cavity proved easiest to operate.	As Ge Sb Sn	234.984 303.906 259.806 317.502	1 ppb at 3σ level for all cavities.	94
Beenakker TM_{010} cavity viewed axially He plasma.	10' x 1/8"i.d., stainless steel Tenax G.C.	Haloforms in drinking water.	Compared MIP with HECD. Found MIP was preferable since it gave uniform molar response and also gave	Cl Br I	481.0 470.5 206.2	1 ppb.	119 contd.

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
			selective detection.				119
Mixed Ar (400 ml min^{-1}) and He (300 $cm^3 min^{-1}$) plasma, 110 W for forward power. Evenson ¼λ cavity.	3'x4.7 mm. i.d. Polypenco Nyla-flow tubing packed with Chromosorb 102 60/80 mesh $T_c = 23 \pm 3°C$.	Whole blood, enriched flour NBS orchard leaves (SRM 1571).	Hydrides trapped on liq. N_2 cooled condensation tube packed with glass helices prior to separation on GC column.	As Ge Se Sb Sn	193.7 303.9 196.0 259.8 317.5	7 ng 3 " 25 " 10 " 40 "	95

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
					simultaneous		
See ref. 95.	See ref. 95.	NBS orchard leaves; hydride generation.	Elements except Ge determined both sequentially and simultaneously. The former giving lower detection limits.	As	235.0	70 ng	
				Se	196.0	600 ng	
				Sb	259.8 (2^o order)	20 ng	
				Sn	317.5 (2^o order)	130 ng	
					(for sequential see ref .95)		96
See ref. 121.	See ref. 121.	H emission from organic compounds.	Characterization of emission from atomic H in MIP accounts for nonlinearity observed.	H	656.28		120

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
He plasma, TM_{010} cavity viewed axially.	12.5 m fused silica WCOT, SP2100, capillary column 0.2 mm i.d., T_c=80-116°C at 4°C min^{-1} to170° 0.1μl injections. Column passed to within 5 mm of plasma.	Toluene solutions of volatile organometallic compounds. $[CpV(CO)_4]$, MMT, $[Cp_2Fe]$, $[Cp_2Ni]$, $[CpCo(NO)(CO)_2]$ $[(CH_3)_5CpCo(CO)_2]$	The low volume of GC^2 column (≏80μl) is ideally compatible with MIP. Specificity of detection aids identification of the unresolved $[Cp_2Ni]$ and $[CpCr(NO)(CO)_2]$ complexes.	C Cr Co Ni Mn	247.9 267.7 240.7 231.6 257.6		103
He plasma TM_{010} cavity viewed axially. He=450$cm^3 min^{-1}$.	OV-225 SCOT, 100m x 0.25 mm i.d. He = 4cm^3/min.	Friedel-Crafts catalysed alkyl group redistribution reaction of methyl-	35 redistribution products are formed, due to requirement to vent	Si	251.6		104 contd.

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	T_I = 210°C T_c = 40°C then 4°min^{-1} T_{in} = 250°C	ethyl-n-propyl-n-butyl silane.	the solvent the low MW products which elute with the solvent are not recorded.				104
He atmospheric plasma, using TM_{010} cavity, 85-90W forward power.	Glass, 1.5mm x 4mm. i.d. 2% OV-101 on 80/100 mesh Chromosorb WHP. T_c = 238°C. He = 60cm^3 min.$^{-1}$	PBB and related compounds.	Not as sensitive as the ECD but offers element selectivity.	Br	478.55	1 ng.	122

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
He plasma in a surfatron cavity (see ref. 107)	30 m capillary column coated with OV-101 methyl silicone He = 5.9ml min^{-1} T_I = 275°C. T_c = 250 for pesticides.	Pesticides.	The surfatron He plasma gives slightly higher detection limits than those obtained with other cavities.	C Cl Br I	247.8 479.5 481.0 470.5 206.2	0.5 to 20 ng.	106
See refs. 97, 119.	See refs. 97, 119.	Aqueous chlorination products of humic and fulvic substances.	In addition to trihalomethanes significant number of chlorinated phenolic cpds were found.	Cl	479.5		124

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
See ref. 125.	See ref. 125.	Selenium bio-methylation products from soil and sewage.	$(CH_3)_2Se$, $(CH_3)_2Se_2$, and $(CH_3)_2SeO_2$ found.	Se		20 pg for $(CH_3)_2Se$.	123
TM_{010} cavity, He plasma, 90W forward power O_2 as scavenger. He = 40-70cm^3-min^{-1}.	15.2m x 0.508 mm. i.d., SCOT column packed with finely ground diatomaceous earth on silica support coated with m-bis (m-phenoxy-phenoxy) benzene and Apiezon L,	Hydrocarbons, $(CH_3)_2Hg$, $(C_2H_5)_2Hg$.	FID proved 50X more sensitive than MIP for C (at 193.1 nm). Both had the same sensitivity for (C_2H_5)-Hg. The MIP was 2X as sensitive as FID for	C	193.1 and 247.9	3.8×10^{-12} g s^{-1}	
				Hg	254.3	9.1×10^{-12} g s^{-1}	102 contd.

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	He = 0.5-8cm^3 min^{-1}. T_c = 90°C		$(CH_3)_2Hg$ using Hg specific detection.				102
TM_{010} cavity He plasma		Organic compounds; elemental analysis.	Linear ranges of 3 orders of magnitude for all elements.	C	193.1	3×10^{-11} mol l^{-1}	
					247.9	4 " "	
				H	486.1	2×10^{-9} "	
				Cl	479.5	2×10^{-10} "	
					481.0	3×10^{-10} "	
				Br	470.5	6×10^{-11} "	
					487.5	10^{-10} "	
				I	516.1	2×10^{-11} "	
					206.2	3×10^{-11} "	
				S	545.4	8×10^{-10} "	126

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
¼λ Evenson low pressure (40T). TM_{010} atmospheric pressure. Ar and He plasmas. The latter viewed axially.		n-hydrocarbons $C_4 - C_7$.	With the aid of a reference compound it is possible to determine ratio formulae, however results are inadequate for unknown compounds.	C H	C = 247.86 H = 656.28 C_2 = 576.52 CH = 431.42	TM_{010} He Ar C 0.67 0.2 H 0.13 4.7 ¼λ Evenson He Ar C 0.44 0.35 H 0.16 0.36 in ng s^{-1}.	84
Atmospheric pressure He plasma in a TM_{010} cavity. Background correction by quartz refractor	SP-2100 WCOT fused silica column 12.5m x 200μm i.d., and 30m x 350 m i.d. OV-101 SCOT	Trialkyllead chlorides in spiked tap water samples.	Gas switches interface illustrated which prevents the solvent extinguishing the	Pb C	405.8 247.9	10-30ppb	101 contd.

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
plate.	glass column.		plasma linear from 10ppb to 10ppm.				101
TM_{010} cavity. Atmospheric pressure, He plasma, viewed axially.	12.5m x 0.2mm. i.d. SP2100 fused silica WCOT capillary column. T_c = 60°C - 104°C at 4°C min^{-1}. 0.1µl injections 100:1 split. For boration studies.	Detection of volatile B compounds from the pyrolysis of Dexsil series carborane silicone polymer, and from boration of diols with n-butylboronic acid.	H_2 doping of the plasma inhibits formation of oxides or silicates, promotes boron hydride formation and the population of B atomic, rather than ionic, states.	B	247.77		105

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
TM_{010} cavity. Atmospheric pressure; He plasma, 75W forward power; He = 80 $cm^3 min^{-1}$.	Glass 3m x 3mm i.d. columns packed with either: 3% OV17 on 80/-100 mesh Shimarate W, 10% Carbowax 6000 on 30/60 mesh Shimarate TPA, or Porapak Q, 80/-100 mesh. T_I = 190°C T_{in} = 190°C.	Various organic compounds.	Relative sensitivities for C and H in different compounds were not the same. Attributed to incomplete fragmentation in low power plasma used.	H	656.279	6.2 $pg.s^{-1}$	
				C	193.091	8.8 "	
				F	685.602	1.8 "	
				Cl	479.454	5.4 "	
				Br	470.486	6.3 "	
				I	206.238	6.6 "	
				S	545.388	39.0 "	

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Atmospheric pressure, He plasma, TM_{010} cavity. See ref. 101.	12.5m SP2100 fused silica capillary column. 100:1 split ratio. T_c = 40°C-100°C at 5°C min^{-1} 0.01 μl sample.	Tetraalkyllead compounds in petrol.	Demonstrates advantage of element specific detection by comparison of Pb and C responses.	Pb C	283.3 247.86		99
Atmospheric pressure, He plasma, TM_{010} cavity. 75W forward power, 12W reflected.	1m x 3mm i.d. glass column, 15% DC-200 on 80/100 mesh Uniport B and 3% OV-17 on 80/-100 mesh Uniport	F in urine.	F^- extracted with TCMS and converted to TMFS in toluene Linear over 4 orders of magnitude.	F	685.6	7.5 pg.s^{-1}	128 contd.

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	HP. He = 80 ml min^{-1}.						128
Atmospheric pressure, He plasma, TM_{010} cavity. See ref. 101.	12.5m x 200 μm i.d., SP2100 fused silica WCOT. Terminated within 1-5 mm of cavity wall.	Redistribution reactions for Ge, Sn and Pb alkyls. Pb alkyls in gasolines.	H_2 doping of He enables plasma to withstand 1-2 ng s^{-1} throughputs of Pb, Ge or Sn. Linear over 3 orders of magnitude.	Ge Sn Pb	265.1 284.0 283.3	3.9 pg 6.1 pg 0.71 pg	100

2.2.1.2 Inductively Coupled Plasma Emission Spectroscopy

The inductively coupled plasma originally developed in the early 1960's has gained much in popularity over recent years (131). The plasma torch consists of three concentric tubes, the outer two are usually fabricated in quartz. The outer gas flow is delivered tangentially and may be of either argon or nitrogen; in the latter case it serves only to cool the outside of the plasma and protect the torch. The intermediate flow may be omitted if argon is used in the outer flow, as the outer gas can serve to propagate the plasma. Alternatively, an intermediate tangential flow of argon is used as the plasma gas. The central injector flow conventionally consists of argon plus the analyte aerosol. The torch is situated in an induction coil, typically two or three turns of copper tubing (ca. 6 mm. i.d.), which is coupled to a radio frequency generator giving 1 - 30 kW of output at 5-40 MHz. The usual combination is a few kilowatts at 27.12 MHz. When the power is switched on, an alternating magnetic field is established having field lines running axially through the coil. The plasma is not established until charged particles, to which the power may couple, are present.

The flowing argon stream is thus seeded, using a Tesla discharge, with electrons. The free electrons are accelerated by the field rapidly reaching ionizing energies, thus causing further argon gas breakdown and an avalanche effect. The induced magnetic field causes the electrons and ions to flow in closed circular horizontal paths. The neutral argon gas is heated by collisional energy exchange with

the charged particles and a white hot fireball produced. The argon ICP is another plasma which is not in LTE; the gas temperature is less than the excitation temperature which is less than the ionization temperature. This has led to the suggestion of a non-thermal excitation mechanism (132) involving collisions with argon metastables known as Penning ionization. This is particularly attractive since the excitation energies of the metastable argon levels of 11.55 and 11.71 eV (132) correspond well with the excitation energies of singly ionized species found in the plasma.

The high capital cost of ICP instrumentation and also the high running costs have resulted in its use mainly as a multi-element excitation source for routine analysis. As a consequence the use of the ICP as a detector for GC, Table 2, has been sparse; however, due to its much higher gas temperature compared to the MIP it can withstand organic solvents more readily and perhaps more use of this emission source will be made in the future.

The initial coupling of GC to ICP was by two groups: Windsor and Denton (133-135) in Arizona, and Sommer and Ohls (136, 137) in Dortmund. The former group showed the capability of ICP OES for the elemental analysis of organic compounds (133) using an all-argon plasma. This capability was then utilized in a GC-ICP coupling (134) for simultaneous multi-element elemental analysis of organic and organometallic compounds. The natural extension of this work was thus empirical formula determinations. Windsor and Denton (135) used carbon, hydrogen and halogen ratios to find the empirical formula of various organic compounds; however, while the technique provided the

ability to analyse for a large number of elemental constituents, usable lines for oxygen and nitrogen were not found. Sommer and Ohls (136) used both all-argon and the nitrogen cooled plasmas for the determination of tetraalkyllead compounds in various petrols by monitoring the lead emission. The same authors (137) determined nickel and zinc as diethyldithiocarbamates, using a nitrogen cooled plasma. Fry et al. (138) investigated a large number of fluorine atom lines for selective detection of various fluorine-containing organic compounds, using off-line correction to remove interference from the solvent emission. Brown et al. (139) monitored near infra-red oxygen emissions to enable oxygen-specific detection. The determination of volatile hydrides of arsenic, germanium and antimony by GC-ICP, using a sequential slew-scanning monochromator (140) demonstrates how the use of chromatography enables rapid multi-element analysis using a monochromator. Table 2 lists applications which have appeared to date.

Table 2. Coupled Gas Chromatography - Inductively Coupled Plasma Optical Emission Spectroscopy

Detector	Chromatography	Matrix	Sample treatment/Comments	Element	Wavelength (nm)	Detection Limit	Reference
All Ar plasma observations made 9mm above load coil. Computer controlled data acquisition system. See ref. 133.	6' x 1/8"packed with 8% Carbowax 1540 on 80/100 mesh fire-brick.	Elemental analysis of various organic compounds.	Used single- and multi-channel monochromators. Using the latter monitored C and H channels for TMT, toluene and p-xylene.	Br	700.57	0.2 mg	
				C	247.86	12 ng	
				Cl	725.67	7 μg	
				F	634.67	1 mg	
				H	656.28	5.5 ng	
				I	206.16	24 ng	
				Si	251.61	0.8 ng	
				Fe	371.99	5.9 ng	
				Pb	217.00	33 ng	
				Sn	284.00	0.9 ng	134
All Ar plasma See refs 133, 134. Power = 0.8 kW Coolant = 12 l.-min^{-1}	See ref. 134.	Halogen containing hydrocarbons.	Elemental ratio determinations for each peak typically 200 elemen-	C			
				H			
				I			
				Cl			135 contd

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Plasma = 0.5 l.-min^{-1}. Sample = 0.9 l.-min^{-1}. Makeup = 0.9 "			tal ratio determinations were achieved to yield an average figure.				135
Uses both high power Ar/N_2 and low power Ar/Ar plasmas.	SP1000. T_c = 140°C(si) T_c = 150°C(Pb) N_2 = 30 cm^3-min^{-1}.	$Si(OC_2H_5)_4$ TML,TEL in petrols.	Looked at lead in petrols using standard addition also TML/TEL ratio and C background at 220.35 nm.	Si Pb	212.4 288.1 220.35		136 and 137

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Ar/Ar plasma 1.75 KW forward power. Used elongated torch, observation zone 5.5mm above load coil.	10% Carbowax 20M on Chromosorb P 80/100 mesh. Ar= 25 $cm^3.min^{-1}$ T_c= 100°C T_{in}= 100°C	Monitored near IR oxygen emissions for various gases and organic liquids.	Studied effect of varying various plasma gas flows on signal and background levels.	O	777.194	650 ng	139
All Ar plasma.	6'x 1/8" packed with Amine 220 T_c= 105°C Ar= 25 cm^3 min^{-1} sampling loop used.	Separation of benzenetrifluoride and o-fluorotoluene	F/C selectivity of 1.0 at 685.602 nm without background correction. By using "off line" correction solvent peak disappears.	F	Considered 56 lines in the region 350 to 895 nm.	1 μg	138

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
All Ar plasma with slew scanning monochromator. 1 KW forward power. Observation 15mm above load coil.	3.5' x 3mm i.d. Chromosorb 102 at ambient temperature.	Hydrides generated, cold trapped and passed through column into plasma.	Sequentially eluting hydrides monitored Linear over 2-3 orders of magnitude.	Ge As Sn Sb	303.9 278.0 317.5 287.8	4 ng Ge 50 ng As and Sb	140

2.2.1.3 Direct Current Argon Plasma Emission Spectroscopy

The DCP is essentially a direct current arc struck between two or more electrodes and stabilized by a flow of inert gas. The development of the DCP has been reviewed by Keirs and Vickers (141) and Greenfield (142). The most recent and perhaps successful DCP system is a commercial three-electrode system which produces a stable inverted 'Y' shaped discharge (143). It is unlikely that the sample actually penetrates the highest temperature part of the discharge (7000-9000 K). In any case the high plasma continuum prohibits observation in this region, which is made instead in the angle of the 'Y', the excitation temperature of the plasma being about 5500 K.

In the few reported couplings of GC with DCP OES, Table 3, the group at Amherst have been dominant (61, 99, 104, 144-146). They found it possible to use argon, helium or nitrogen as a carrier gas (145), although in certain spectral regions interference from cyanogen bands could occur with nitrogen. The use of a sheathing gas, heated to prevent sample condensation around the injector nozzle, was found to increase sensitivity (144, 145). The coupled technique has been used as an element-selective detector for: manganese as the cyclopentadienyltricarbonyl derivative (144); copper, chromium, nickel, palladium and zinc chelates (145); iron in ferrocene (146), and various group IV metals in an interesting study of Friedel-Crafts catalysed alkyl group redistribution reactions (104). Treybig and Ellebracht (147) utilized a vacuum ultraviolet plasma spectrometer (148, 149) for sulphur-specific detection which compares favourably with MIP detection and has the advantage that solvent venting is not required. The applications are summarised in Table 3.

Table 3. Coupled Gas Chromatography - Direct Current Plasma Optical Emission Spectroscopy

Detector	Chromatography	Matrix	Sample treatment/comments	Element	Wavelength (nm)	Detection Limit	Reference
Prototype spectraspan III dc plasma echelle spectrometer.	6'x 1/8" i.d. stainless steel 2% Dexsil 300 GC on 100/120 mesh Chromosorb 750. 1:1 split with FID. $T_c = 130^oC$ $T_I = 160^oC$ $T_{in} = 170$ He= 25 $cm^3 min^{-1}$	MMT in gasoline, standards in isooctane. Eymantrene as internal standard.	Only sample modification required was addition of the internal standard. 3 min. analysis time. Upper limit of linear range was 340 ng.	Mn		3 ng.	144
See ref. 144. Details of heated interface design	6'x 1/8" i.d., 3% Dexsil 300 on 100/120 mesh	$Cr(tfa)_3$	Sheathing gas around the issuing g.c. efflu-			Cr = 34 $pg.s^{-1}$ Cu=5.6 $pg.s^{-1}$ Ni=320 $pg.s^{-1}$	145 contd.

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
given.	Chromosorb 750.		ent prevented			Pd =120pg.s^{-1}	
Dual detection	T_c= 170°C		excessive dif-			C= 0.28pg.s^{-1}	
with FID used	He= 60 cm^3min^{-1}		fusion as the				
sheathing gas	T_c= 220°C	$Cu(en)(tfa)_2$	sample trav-				
heated to 230°C	6'x1/8"i.d.2.5%	$Cu(pn(tfa)_2)$	elled into the	Cu	324.7		
to prevent con-	Dexsil 300 GC	$Ni\ pn(tfa)_2$	plasma from	Ni	341.7		
densation of	T_c= 230°C	$Pd\ pn(tfa)_2$	the interface	Pd	340.4		
eluents.	T_c=280°C	$Zn\ (dtc)_2$	tubing.	C	247.8		
T_{in}= 230°C	6'x1/8"i.d.3.2%	$CpCr(NO)(CO)_2$	Linear from 2-	Cr	267.7		
	Dexsil 300 GC on	benzene-	150 ng for Cr.				
	100/120 mesh	chromium					
	Chromosorb 750	tricarbonyl.					
	T_c= 190°C						145
							contd

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	6'x 1/8"i.d., 10% SE-30 on 60/80 mesh Gas Chrom. S. T_c = 170°C.	C_{10},C_{12},C_{14}, and C_{16} hydrocarbons.		C	247.8		145
For spectrometer and interface see ref. 167. Except used 3 electrode jet rather than a 2 electrode one. Ar flow rates: Sheathing = 1.42-1.65 1 min^{-1} Cathode = 2.0	6'x 1/8" stainless steel, 5% OV-101 on 100/-120 mesh Chromosorb 750. He= 40 $cm^3 min^{-1}$ T_c= from 80°C to 6 or 8°C min^{-1} T_I= 210°C T_{in}= 220°C	Friedel-Crafts catalysed alkyl group redistribution reactions.	Redistribution reactions of the following pairs: $^{n}Pr_4Sn$+Et_4Pb Et_4Sn+$^{n}Bu_4Ge$ $^{n}Pr_4Si$+$^{n}Bu_4Ge$ $^{n}Bu_4Ge$+Et_4Pb Vn_4Si+Et_4Sn Vn_4Si+$^{n}Bu_4Ge$ studied.	Si	251.6		104 contd
				Ge	265.1		
				Sn	286.3		
				Pb	368.3		

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
1. min^{-1} Anode = 1.3 l.-min^{-1} Current = 7 A Voltage = 40 60 V.	Nickel tubing 1m x 1/8", 3% OV-201 on 100/- 120 mesh ultra- bond 20 M. He= 40 cm^3min^{-1} T_c= from 80°C at 8°Cmin^{-1} T_I= 210°C T_{in}= 220°C		Formation of PbR_3Cl and SnR_3Cl by reaction with $AlCl_3$ studied.	Pb Sn	368.3 286.3		104
See refs. 104 and 145.	100'x 0.03"i.d. stainless steel PLOT OV-101 T_c= 170°C.	Ferrocene and halo- derivatives.	Paper contains many other orga- nometallic separations, however the	Fe	372.0		146 contd.

Detector	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
			detector used is the FID.				146
Vacuum UV spectrometer with spectrametrics dc plasma.	122 cm x 2 mm i.d., Porapak super Q.	CS_2, thiophene 3-methylthiophene.		S	180.7	0.3 ng S-s^{-1}.	
	183 cm x 2 mm i.d., 3% OV-101 on Chromosorb W HP, 80-100 mesh. N_2= 80 $cm^3 min^{-1}$	hexanethiol benzenethiol methylsulphoxide.					147.

2.2.2 Atomic Absorption Spectroscopy

Atomic absorption follows an exponential relationship between the intensity of transmitted light, I, and absorption path length, L, similar to Lambert's law in molecular spectroscopy.

$$I = I_o \exp(-k_\nu l) \qquad \ldots (2.6)$$

where I_o is the intensity of the incident light and k_ν is the absorption coefficient at the frequency ν. For quantitative spectroscopy the absorbance, A, is defined by:

$$A = \log (I_o/I) \qquad \ldots (2.7)$$

thus

$$A = k_\nu l \log e$$

$$= 0.4343\ k_\nu l \qquad \ldots (2.8)$$

It is possible to demonstrate (150) from classical dispersion theory that in practical terms k_ν is proportional to the number of atoms per cubic centimetre in the flame, i.e. absorbance is proportional to analyte concentration.

Atomic absorption corresponds to transitions from low to higher energy levels, hence, the degree of absorption will be dependent on the low level population. When thermodynamic equilibrium prevails, the population of a given energy level is given by the Boltzmann law - see section 2.2.1. The population of the ground state is generally much greater than higher energy levels and as a result absorption is greatest for resonance lines which result in transitions from the ground state.

The exploitation of atomic absorption was late in arriving due to the extreme narrowness of atomic lines (typically about 0.002 nm). Thus the amount of radiation isolated by a conventional monochromator is not significantly reduced by the narrow absorption signal if a continuum source is used. The considerable contribution made by Walsh (151) to atomic absorption spectroscopy was to use a line source to replace the continuum. Since absorption and emission lines have the same wavelength the narrowness of the absorption line is a positive advantage. Thus overlap of an absorption line of one element with an emission line of another is negligible and hence only resolution from other lines in the lamp, e.g. filler gas lines, is required. This 'lock and key' mechanism is responsible for the greater selectivity of AAS over AES. Atoms may be generated for AAS in a variety of ways of which flames and electrothermally heated furnaces are the two most popular. Coupling of these two atom cells to GC is reviewed in the next two sections.

2.2.2.1 Flame Atomic Absorption Spectroscopy

The use and characteristics of flames used for absorption spectroscopy have been widely discussed (152-154). Premixed laminar flames are in most common usage since they offer high temperature with relatively low background emission, have well documented chemical compositions and are easily reproduced (154). For many elements the air/acetylene flame produces sufficient atomization to enable good sensitivity with freedom from inter-element interferences. It is not just the enthalpy of the flame which decides the degree of atomization but also the flame chemistry. This is evidenced by the fact

that the elements, Bi, Ca, Cr, Ga, Sn, and Sr, are atomized substantially more in the hot reducing nitrous oxide/acetylene flame and the cool hydrogen/air flame than in either the hot nitrous oxide/hydrogen flame or the cooler air/acetylene flame (155).

For coupled GC-AAS (156-160) systems, see Table 4. Flame atomization offers the advantages of continuous operation, simplicity and low cost instrumentation. One of the main disadvantages of FAAS compared to electrothermal atomization, ETA, for solutions, is that whilst the latter atomizes the whole sample in the former the nebulization efficiency is low, about 10%. With GC-FAAS this disadvantage is unimportant, since the analyte is in the gas phase prior to entry into the atom cell. An additional disadvantage is that FAAS normally has higher detectability than ETA AAS due to the shorter atomic residence times in the flame.

The simplest way of interfacing a gas chromatograph with an atomic absorption spectrometer is to pass the column effluent via an interface tube into the nebulization chamber, to be swept by the oxidant and fuel gases into the flame. The first reported GC-FAAS coupling by Kolb et al. (161) used this method to determine tetraalkyllead compounds in petrol with an air/acetylene flame. This interfacing method has been utilized by various authors (18, 162-166). Morrow et al. (162) used the nitrous oxide/acetylene flame for the silicon specific detection of silylated alcohols and an air/acetylene flame for atomic emission detection of the same species. A similar coupling was used to determine lead in petrol (18, 163-165), and in the atmosphere (18, 163). Hahn et al. (166) used such an arrangement to

determine As, Ge, Se and Sn, after generating hydrides, using a hydrogen diffusion flame. Coker (167) realised that dilution of the sample and excessive peak broadening caused by passage through the nebulization chamber could be avoided. He passed the chromatographic effluent into a manifold just below the burner slot and achieved better detection limits for tetraalkyllead compounds in petrol than the previous couplings. Wolf (168, 169) used a similar coupling to specifically determine chromium in standard orchard leaves after chelation with trifluoroacetylacetone, as did Chan (170) when investigating tetraalkyllead ratios in petrols from varying sources. Reports arising from the work described in this thesis (159, 171, see Chapters 4 and 5), have emphasized that in order to enable true trace level determinations by GC-FAAS, the residence times of atoms in the flame must be increased. This has been achieved by using a flame heated ceramic tube suspended over a flame in various configurations (159, 171). The need for low level detection by GC-AAS led to the consideration by various authors (see section 2.2.2.2) of electrothermal atomizers.

2.2.2.2 Electrothermal Atomization Atomic Absorption Spectroscopy

The theory and practice of electrothermal atomization for AAS has been reviewed by Fuller in a monograph (172) and in numerous books (e.g. 150, 154, 173). The main advantages of ETA over flame atomization for coupled GC-AAS are claimed to be increased sensitivity, safety and the possibility of unattended operation. The increased sensitivity arises because electrothermal atomization does not suffer from the poor nebulization efficiency, rapid dilution in the expanding flame gases and short atomic residence times which beset flame

atomization. Improvements in detection limits with electrothermal atomization over flame atomization are typically in the range 100-1000-fold for solution work (173). The use of explosive gases is avoided, less toxic fumes are produced, thus safety is increased and the atomizer may thus be left unattended. Commercial electrothermal atomizers, mainly graphite furnaces of various designs, are constructed to handle small, 10-100μl, discrete condensed phase samples and the heating of such devices is typically not continuous. Thus modification of the atom cell is required before it can accept a continuous gas stream from a chromatograph.

The electrothermal devices used in coupled GC-AAS, see Table 4, fall into three main categories:

i) home made electrothermally heated quartz or ceramic tubes;
ii) commercial graphite furnaces;
iii) commercial cold vapour mercury analyzers.

This latter atom cell has been used for mercury specific detection of organomercurials in various samples. Hey (174) passed the effluent from the chromatograph into a continuous wet chemical reduction cell the reduced Hg(0) being swept into the cold vapour absorption cell of a commercial system (MAS 50, Colman Instruments). Other authors (175-179) used a flame ionization detector flame to atomize the organomercury species which then passed into the same cell. Dressman (175) used this method to speciate dialkylmercury compounds in spiked river waters. Blair et al. (178) also used this method in a study of mercury transformations in aquatic environments. Gonzalez and Ross (180) used a quartz combustion furnace prior to the detector to

determine methyl- and ethyl-mercury chlorides in fish tissues with better selectivity towards mercury than the electron capture detector exhibits towards the organomercury chloride.

The use of an electrothermally heated silica tube as an atom cell for coupled GC-AAS was pioneered by Chau et al. (181). The furnace was heated to around 1000°C with air and hydrogen flowing through and used a selenium specific detector for the separation of dimethyldiselenium and dimethylselenium (181). Chau, with a variety of coworkers, then used this coupled technique for numerous environmental applications (18, 25, 33, 181-187). This group developed the technique for metal specific detection of organolead in the atmosphere (163, 187), the aquatic environment (184, 185) and for methylation studies of lead (18, 33, 183), tin (25), arsenic, mercury and selenium (18). Thompson (20) utilized a similar atom cell to study methylation pathways in coastal sediments as have Brueggemeyer and Caruso (188) for the determination of inorganic lead in aqueous samples after methylation of the extracted dithiocarbamate lead complex. Van Loon and Radziuk (189-191) developed a silica 'T' tube for coupled GC-AAS. This low cost arrangement had the chromatographic column contained in the long arm of the 'T', the effluent then passed into the cross piece atomizer purged with flows of hydrogen and nitrogen. The system was used as a metal specific detector for organoselenium compounds (189) and in the study of organoselenium transpiration by Astragalus racemosus (190, 191). Bye and Paus (192) used an electrothermally heated quartz furnace to atomize organomercurial compounds prior to their detection in an unheated silica cuvette. In a comprehensive study of various tetraalkyl, methyl- and ethyl-tin chlorides (59)

Burns et al. used an electrothermally heated quartz tube as atomizer. They found detection limits were drastically lowered if the hydrides were generated prior to atomization. Radziuk et al. (193) compared the suitability of various atom cells for coupled GC-AAS, with the graphite furnace proving the most sensitive for lead; indeed, it gave a factor of fifty increase in response when compared to a simple Kolb type flame coupling.

The first GC coupling to a commercial graphite furnace was rather crudely achieved by Coker (194). The end of a tungsten transfer line was passed through an enlarged hole in the graphite tube so that the effluent impinged on the hot tube wall. Parris et al. (195) considered the effect of using pyrolytically coated, alumina lined and standard graphite tubes at various atomization temperatures with and without hydrogen (10%) added to the chromatographic effluent. The best detection levels were achieved for As, Se and Sn, using standard graphite tubes with hydrogen added to the effluent flow and an atomization temperature of 1800°C. Robinson et al. (196) passed the chromatographic effluent through a graphite electrode into the optical path of a home made atomizer which was kept at 2000°C throughout the chromatographic run. This atomizer was used for lead specific detection of tetraalkyllead compounds in petrol (196) and in a study of the degradation of TEL in sea water (197). Bye and Paus (165) found graphite furnace atomization was 100-fold more sensitive than flame atomization for the determination of TML in petrol. The determination of tetraalkyllead compounds in various matrices has again proved very popular; for example, Cruz et al. (198) in fish, water, sediment and vegetation samples. The group in Antwerp developed the most sensitive

GC-GFAAS coupling for tetraalkyllead compounds (199) and used it to determine these compounds in petrol (34, 199), the atmosphere (34, 200, 201) and in a preliminary study of their degradation in river water (34). Determination of another "anti knock" petrol additive, methylcyclopentadienylmanganese tricarbonyl, in the atmosphere, was achieved by Coe et al. (202) down to very low levels, 0.05 $ng.m^{-3}$. Winefordner and coworkers (203) have demonstrated a novel method of avoiding matrix interference by selective volatilization using coupled high temperature (ca. 2093 K) GC-AAS. They used a molybdenum column/atomizer for the separation of sodium, copper, manganese and magnesium ions with excellent correlation of analytical signals for each metal in pure and mixed solution. This work opens a new area of application for GC-AAS, since prior to this the only separation of analytes in inorganic matrices was for elements which formed volatile hydrides or volatile chelates. This technique offers a possible method for separating interfering concomitants from the analyte prior to atomic spectroscopic analysis.

Table 4. Coupled Gas Chromatography - Atomic Absorption Spectroscopy

Atomizer	Chromatography	Matrix	Sample treatment/comments	Element	Wavelength (nm)	Detection Limits	Reference
Flame AAS, GC effluent passed via a heated tube into the nebulization chamber.	2m x 2mm i.d., 10% Apiezon M on Chromosorb R. N_2 = 40 ml-min^{-1}. T_c = 150°	Pb alkyls in petrol, TML and TEL.	First paper to describe GC-AAS coupling for element specific detection. Linear range 50-700 ppm.	Pb	217.0		161
Flame AAS, N_2O/-C_2H_2 FAES air/-C_2H_2 flame. Coupling was through the nebulization chamber.	6' x 0.25" i.d. steel column, 20% SE30 on 30/60 mesh chromosorb W. He = 100 ml.-min^{-1}	Silylated pyridine solutions of n-alcohols C_1-C_7.	Interface tube, stainless steel (0.0345" i.d.) heated in excess of T_c. AAS 4-20 μg AES 3-100 μg	Si	251.6	AAS 0.11 μg AES 0.72 μg	162 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	T_c = 130°C.		Linear range.				162
Using cold vapour analyzer.		Organomercury compounds.	Passed GC effluent into a continuous wet chemical reduction vessel; Hg then flushed into cold vapour cell. Linear up to 10 μg.	Hg	253.7	50 ng	174
As ref. 174	Glass 6' x 0.25" column, 5% HIEFF-2AP	Alkyl mercury compounds in fish tissue	GC effluent passed into a quartz tube	Hg	253.7	2.5×10^{-11} g of MeHgCl gives 1%	180 contd.

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	on Chromosorb WHP, 80/100 mesh. N_2 = 120-ml.min^{-1}. T_I = 200°C T_c = 170°C T_{in} = 200°C	MeHgCl and EtHgCl.	combustion furnace (780°C) prior to passing into the cold vapour cell. Linear up to 45 ng.			absorption	180
See ref. 174.	6' x 2 mm i.d. glass column, 5% DC-200 + 3% QFI on 80/-100 mesh Chromosorb Q, T_c = 70°C hold 2 min then 20° Cmin^{-1} to 180°C	Dialkyl mercury compounds in spiked river waters.	The effluent was passed through the FID to combust the mercury compounds prior to entry into the cold vapour analyzer	Hg	253.7	0.1 ng	175

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
See ref. 174.	See ref. 175.	Dialkyl mercury compounds, Me_2Hg, Et_2Hg, $^nPr_2Hg$, $^nBu_2Hg$.	See ref. 175. Linear from 0.05 ng to 100 ng.	Hg	253.7	0.02 ng for Me_2Hg	176
See ref. 174.	See ref. 175.	Dialkyl mercury compounds.	See ref. 175. Linear from 0.05 to 100 ng for Me_2Hg and Et_2Hg.	Hg	253.7	0.02 ng for Me_2Hg	177
See ref. 174.	6' x 0.125" glass column, 5% SP2100 + 3% SP2401 on	Mercury compounds involved in transformations of	Study of methylation pathways in microorganisms	Hg	253.7		178 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	80/100 mesh Supelcon AW-DCMS. N_2 = 20 ml.min^{-1} T_c = 60°C hold 2 min then 32°C min^{-1} to 180°C.	microorganisms, in soils and sediments.					178
Air/acetylene flame.	3m x 3mm Teflon tube. N_2 = 40 ml.min^{-1} T_c = 110°C.	Pb alkyls in gasoline samples.	Effluent passed from GC into spray chamber. 5 cm burner. Linear from 0.2 to 40 μg.	Pb	217.0		164

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Graphite furnace kept at 2700°C with background correction.	6'x 5/16"i.d.on glass column, 4% SE-30 + 6% OV210 on Gas Chrom Q. Ar = 50 $ml.min^{-1}$ T_c = 150°C 2.0 µl injections.	Pb alkyls in gasoline.	10cm W transfer line connected into an enlarged hole in graphite tube.	Pb	217.0	10 ng Pb	194
Electrothermally heated silica tube (60mm x 7mm i.d., T = 1000°C) Furnace gases:	1.8m x 6mm glass column, 3% OV-1 on Chromosorb W 80/100 mesh. T_c = 40°C hold	Me_2Se and Me_2Se_2 in synthetic air samples.	Air samples trapped at -80°C on 3% OV-1 on Chromosorb W and desorbed into the GC at	Se	196	0.1 ng Se	181 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
air = 120 ml.min^{-1} H_2= 120 ml.min^{-1}	2 min then 15°C -min^{-1} to 120°C T_I= 225°C		80°C. The trap being heated in a commercial 'toaster'. Linear up to 50 ng.				181
Air/C_2H_2 flame.	3'x 3/16"i.d. steel column, 10% Carbowax 20M on 100/120 mesh Porasil C. H_2= 120 ml.min^{-1} T_c= 130°C Home made column heating system.	Pb alkyls in gasoline.	The effluent from the GC passes into a manifold just below the burner slot which evenly distributes the effluent along the flame.	Pb	283.3	0.2 ppm	167 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	5μl injections.		Linear up to 200 ppm for TML and 1000 ppm for TEL.				167
AAS using an electrothermally heated silica furnace. See ref. 181.	See ref. 181.	TML from methylation of Me_3Pb^+ salts.	Reported that Me_3Pb^+ salts were readily converted to TML by microorganisms in lake water or nutrient medium.	Pb			183

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Air/C_2H_2 flame. All-glass lining for nebulization chamber used to prevent absorption of organo-lead on chamber walls.	1.8m x 6mm glass column, 3% OV-1 on 80/100 Chromosorb W. N_2= 65 ml.min^{-1}. T_c= 40°C for 2 min then 5°C-min^{-1} to 90°C.	Tetraalkyllead compounds in the atmosphere and gasolines.	The air sample was trapped (see ref. 181); passed through nebulization chamber into flame.	Pb	217.0	80 ng	163
Electrothermally heated silica tube. See ref. 181.	Column (see ref. 163) N_2= 70 ml.min^{-1} T_c= 50°C for 2 min then 15°C-min^{-1} to 150°C T_I= 150°C	Tetraalkyllead compounds in the atmosphere.	For sample trap and chromatographic interface see ref. 181. Linear up to 200 ng	Pb	217.0	0.1 ng	187

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Electrothermally heated silica tube. See ref. 181.	1.8m x 6mm, 3% OV-1 on Chromosorb W 80/100 mesh. Lead see 163. Selenium N_2= 70 ml.min^{-1} T_c= 40°C for 2 min then 15°C min^{-1} up to 120°C. T_I= 225°C	Organometallic compounds in liquid or gaseous samples. For gaseous sample trapping method see ref. 181.	Compounds determined were: tetraalkylleads methylseleniums methylarsines, alkylmercury chlorides, and dimethylcadmium.	Hg Pb Cd As Se	253.6 217.0 228.5 193.7 196.0	0.1 ng for each element	
	Arsenic 10% OV-1 on chromosorb W,						182 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	N_2= 30 ml.min^{-1} T_c= 25°C= T_I T_{in}= 100°C Mercury 5% DEGS on Chromosorb W N_2= 80 ml.min^{-1} T_c= 145°C T_I= 150°C T_{in}= 150°C Cadmium N_2= 70 ml.min^{-1} T_c= 70°C T_I= T_{in}= 80°C						182

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
'T' furnace atomizer (900-1000°C; dimensions, 100mm x 20 mm i.d.) flows into atomizer. H_2= 1 l-min^{-1}; N_2= 6 l-min^{-1}. Quartz 'T' furnace, see ref. 189.	122cm x 3mm i.d. i.d. Al tube, 20% polymetaphenylether on 60/80 mesh Chromosorb W, N_2= 23 ml.min^{-1} T_c= 82°C T_I= 180°C See ref. 189.	Dialkylselenium compounds	The homemade chromatographic system was contained in the quartz 'T' arrangement.	Se	196.0	Me_2Se=10ng Me_2Se_2=20ng Et_2Se_2=20ng	189
		Organoselenium compounds transpired by *Astragalus racemosus*.	The transpired compounds were trapped on DC-550 on Chromosorb W in a dry ice bath. and desorbed at 175°C into	Se	196.0		190 and 191 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
			the chroma-tographic column.				190 and 191
Flame, with chromatographic effluent being delivered directly to the burner cavity.	2' x 3mm i.d. Teflon tubing, 10% SE30 on Chromosorb WHP 80/100 mesh. $T_c = 180^{\circ}C$ $N_2 = 65$ ml.min^{-1} 20 μl injection	Inorganic Cr in NBS SRM 1571 Orchard leaves as $Cr(tfa)_3$ chelates.	After a H_2SO_4/H_2O_2 digestion, Cr chelated with Htfa (0.1 ml.) extracted with hexane (0.5 ml) prior to injection. Linear from 0.5ppm to 5ppm Cr.	Cr		1 ng	168

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Electrothermally heated silica furnace, see 181, or directly coupled through the nebulization chamber to an air/C_2H_2 flame, see ref. 163.	See ref. 187.	Tetraalkyllead compounds in petrol and air samples.	For atmospheric sampling see ref. 181. Linear up to 200 ng for furnace.	Pb	217.0	0.1 ng for furnace system.	186
H_2 diffusion flame burning in quartz cuvette. H_2=250ml.min^{-1} Air= 150ml.min^{-1}	6 m. stainless steel column, 16.5% DC-550 on 80/100 mesh Chromosorb W AW DMCS; He = 80 ml.min^{-1}	Reducible As species in natural waters.	The hydrides of the As compounds isolated by cold trapping, passed down a column and into a	As	193.7	0.05 ng for AsH_3	204 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
			furnace. Linear up to 50 ng.				204
See ref. 175.	80cm x 6 mm i.d. glass column, 10% Carbowax 20M on Chromosorb W AW. 5 to 100 μl injections; T_I = 200°C T_c = 60°C for Me_2Hg; 200°C for MeHgCl N_2=15ml.min^{-1} for Me_2Hg	Me_2Hg, MeHgCl		Hg	253.7	10 ppb Hg	179 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	N_2=200 ml.min^{-1} for MeHgCl.						179
Graphite furnace with pyrolytic or alumina lining or standard graphite tubes, at various temperatures with and without Ar/H_2 (90 + 10) flow (20 ml.min^{-1}).	6' x 1/8"i.d. glass column, 5% SP2100 and 3% SP2401 on 80/100 mesh Supelcon AWDMCS T_c = 40°C Ar= 30ml.min^{-1} T_{in}= 100°C	Me_3As, Me_4Sn and Me_2Se in N_2. To stimulate an atmosphere over a lake system.	Best detection levels achieved using standard graphite tubes with an Ar/H_2 flow at 1800°C Linear up to 320 ng As 313 ng Se 363 ng Sn	As Se Sn		5 ng As 7 ng Se 12 ng Sn	195

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Graphite furnace 2000°C. The furnace kept at this temperature throughout chromatographic run.	Teflon column, 8'x 1/8"; 20% TCP on Chromosorb W, Ar = 30ml.min^{-1} T_c = 100°C T_I = 125°C T_{in} = 100°C	Tetraalkyllead compounds in gasoline and the atmosphere.	TEL undetected in all 10 air samples.	Pb	283.3	0.1 ng	196
Air/C_2H_2 flame; see ref. 168.	18" x 3mm i.d. PTFE tubing, 5% SE-30 on Chromosorb P AWDMCS, 80/100 mesh. N_2 = 120 ml.min^{-1} T_c = 160°C	Inorganic Cr in NBS SRM 1571 orchard leaves and SRM1569 brewers yeast as chelates, also Co,Fe and Cu chelates	The chelates determined were: $Co(fod)_3$ $Fe(fod)_3$ $Fe(tfa)_3$ $Cu(ofhd)_3$ Linear from	Cr Co Fe Cu		1.0 ng 80 ng 300 ng 500 ng	169 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	T_I = 150°C.		0.5 to 8.0 µg.				169
Both a flame, air/C_2H_2, the effluent introduced through the nebulizer, and a graphite furnace at 1300°C	20% SE-52 on Chromosorb W, Ar = 90ml.min^{-1} $T_c = T_I$ = 125°C T_{in} = 130°C	Tetraalkyllead compounds in gasoline samples.	The furnace technique was 100X and 75X more sensitive than the flame coupling for TML and TEL respectively.	Pb	283.3	Flame: TML = 17 ng TEL = 81 ng Furnace; TML = 0.12ng TEL = 1.1 ng	165
Hg compounds atomized in electrically heated quartz furnace at 620°C.	10% SP 2300 on Chromosorb W. N_2 = 90 ml-min^{-1}. T_c = 145°C	Alkylmercury compounds in fish.	A rapid method for quantitative extraction of organomercury compounds	Hg	254.0	3.5 ng	192 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	T_I = 200°C		from fish given. Linear up to 120 ng.				192
Electrothermally heated silica tube See refs 181, 187.	See ref. 187.	Tetraalkyllead compounds in water, sediment and fish.	Extraction procedures for three sample types given.	Pb	217.0	Water (200 ml) = 0.5 $\mu g l^{-1}$ Sediment (5g) = 0.01 $\mu g g^{-1}$ Fish (2g) = 0.025 $\mu g g^{-1}$	184
Graphite furnace atomization at 1700°C.	150cm x 6mm i.d., glass column, 3% OV-101 on Chromo-	Tetraalkyllead compound in air.	The Pb compounds from 70 L air samples were trapped	Pb	283.3	40 pg Pb	205 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	sorb W, 80/100 mesh. T_{in} = 80°C T_c = 90°C then 40°Cmin^{-1} to 200°C. Or isothermal at 150°C.		at -72°C on the chromatographic packing.				205.
Various atom cells; air/C_2H_2 flame; flame and electrothermally heated quartz tubes, graphite cup and furnaces.	150cm x 6mm i.d. glass column, 3% OV-101 on Chromosorb W, 80/100 mesh N_2 = 140ml.min^{-1} T_c = 50°C then 40°Cmin^{-1} up to 200°C.	Tetraalkyllead compounds.	If T_{in} > 300°C decomposition of lead compounds occurred and interference from remobilization by the solvent resulted.	Pb	283.3.	30 pg with HGA2100 furnace.	193

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Graphite furnace atomization (see ref. 196) at 1500°C.	18"x1/8" i.d. Teflon column, 20% Ucon Non-Polar on Chromosorb P. Ar = 60 ml.min^{-1}. T_c = 140°C T_I = 150°C T_{in} = 140°C.	TEL in sea water.	Some TEL migrates to surface and evaporates. The majority forms the soluble Et_3PbCl. Evidence of further degradation was found.	Pb	283.3	1 μg ml^{-1}	197
Electrothermally heated silica furnace; see ref. 181.	See ref. 181.	TML in methylation of Pb (II) salts in aqueous solution.	Found a chemical methylation pathway for converting Pb(II) salts	Pb			33 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
			into methyl derivatives.				33
Electrothermally heated silica tube furnace; see refs. 184, 187.	See refs. 184, 187.	Tetraalkyllead compounds in fish, sediment vegetation and water samples.	Samples were analysed for total Pb, volatile Pb tetraalkyllead and hexane extractable Pb.	Pb	283.3		185
Graphite furnace atomizer.	2.3m x 6mm i.d., 3% OV-101 on Chromosorb WHP, 80/100 mesh.	MMT in air samples.	The air samples were collected (see ref. 205) at 70 ml min^{-1} for 8 hours.	Mn	279.5	0.05 ng m^{-3}	202 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	$T_c = 115^{\circ}C$ $T_I = 150^{\circ}C$ $T_{in} = 150^{\circ}C$ $N_2 = 80$ ml min^{-1}						202
Graphite furnace atomization.	Same as ref. 185.	Determination of total, hexane extractable volatile and tetraalkyllead in fish, water sediment and vegetation samples. See ref. 185.	Coupling of chromatograph transfer line to the furnace was via friction fitted Ta connector (193).	Pb	283.3	2ppb hexane extractable, 0.5-1.5ppb volatile, and 0.5ppb tetraalkyllead.	158

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
H_2 diffusion flame, samples introduced through negulizer.	3' x 4.7mm i.d. Polypenco Nylaflow tubing, Chromosorb 102, T_c = 23°C	Determination of As, Ge, Se and Sn after hydride generation and cold trapping of hydrides.	Chromatographic separation allowed manual lamp change and monochromator change between peaks. The overlap of SeH_2 and SnH_4 required their separate detection.	As Ge Se Sn	193.7 265.2 196.0 224.6	As-60ng Ge-260ng Se-100ng Sn-100ng	166

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Graphite furnace atomization at 2000°C. External gas flow of 0.9 $l.min^{-1}$.	Glass column 180cm x 2mm i.d., 3% OV-101 on Gaschrom Q, 100/120 mesh Ar= 30 $ml.min^{-1}$ T_c = 50°C then 20°Cmin^{-1} up to 150°C T_{in} = 200°C	TML and TEL in petrol.	Coupling via 1m x 0.5mm i.d. glass tube. Linear up to 50 ng.	Pb	283.3	40pg TML 90pg TEL	199
Graphite furnace atomization; see ref. 199.	Same as ref. 199; samples desorbed from short glass col column of chro-matographic	Tetraalkyllead compounds in air sampled for 1 hr. at 6 $l.min^{-1}$.	Pb compounds sampled onto glass beads at -130°C. Then transferred to a short column	Pb	283.3	TML = 0.1 ng m^{-3} TEL = 0.3 ng m^{-3}	200 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	material at 90°C into chromatograph.		of chromatographic packing at -196°C.				200
Electrothermally heated quartz tube.	2m x 6mm i.d. glass column, 3% SE30 on Chromosorb GAW DMCS. For R = Me T_c = 120°C N_2 = 16 ml min^{-1} For R = Et T_c = 180°C N_2 = 50 ml min^{-1}	Tetraalkyltin and alkyltinchlorides (R_nSnCl_{4-n}) R=Me and Et.	Owing to column rearrangements all four methyltin compounds cannot be examined. Passed column effluent directly to atomizer and also generated	Sn	286.3	1.0ng for Me_4Sn 2.0 pg for Me_4Sn if hydride is atomized.	59 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
			hydrides prior to atomization. Linear up to 400 ng.				59
Graphite furnace atomization; see ref. 199.	Same as ref. 199.	Tetraalkyllead compounds in air (cf.200), petrol (cf. 199), river and rain water.	Degradation of TML and TEL in river water investigated.	Pb	283.3	TML = 0.2 $\mu g l^{-1}$ TEL = 0.5 $\mu g l^{-1}$	34
Air/C_2H_2flame; effluent from chromatograph introduced just below burner slot.	10'x 1/8" steel column, 20% Carbowax 20M on Chromosorb P N_2= 120ml min^{-1}	Tetraalkyllead compounds in petrol from a variety of sources.	Interface line was 4' x 0.02" i.d. stainless steel.	Pb	217.0		170 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	T_c = 120°C T_I = 140°C T_{in} = 110°C 2 μl injected.		Linear up to 400 ng for TML up to 1400 ng for TEL				170
Electrothermally heated silica furnace (see refs 181, 187) at 850°C H_2 = 150 ml min^{-1}	4' glass column 20% OV-3 on Chromosorb W, 80/100 mesh. N_2 = 80ml min^{-1} T_c = 30°C for 3 min then 20°C min^{-1} up to 110°C. T_I = 85°C T_{in} = 65°C	Methyltin compounds sampled from the headspace above sediment samples in a methylating environment.	Headspace sampling (see ref. 181) Experiments indicated Sn(II) was methylated by CH_3I but Sn(IV) was not.	Sn	224.6	0.1 ng Sn	25

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Electrothermally heated silica furnace; see refs 181, 187.	For chromatographic conditions see refs 163, 182, 187.	Methylated derivatives of As, Hg, Pb and Se.	Study of the effect of pH on methylation in the aquatic environment.	As Hg Pb Se	193.7 253.6 217.0 196.0	0.1 ng of each element.	18
Graphite furnace atomization; see refs 199, 200.	See refs 199, 200.	Tetraalkyllead compounds in the atmosphere Samples taken from rural, urban and gasoline station environs.	Elevated levels of tetraalkyllead compounds were found around gasoline stations and in areas with heavy traffic. Linear up to 50ng.	Pb	283.3	40pgTML 90pgTEL	201

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Electrothermally heated silica tube, see ref. 181.	180cm x 6.4mm, 3% OV-1 on Chromosorb HP 80/100 mesh. N_2 = 25ml min^{-1} T_c = 70°C T_I = 150°C	Tetraalkyllead compounds formed in study of methylation pathways in coastal sediments.	Reported that bioconversion of Pb(II) to TML unlikely in marine environments.	Pb	217.3		20
Electrothermally heated quartz tube (cf. 187) at 980°C.	8cm x 3.2mm i.d. stainless steel column, Porapak Q 80/ 100 mesh. TML was trapped on column and flushed off with N_2	Determination of inorganic Pb in aqueous samples as tetramethyl derivative formed by methylation of the extracted	Methylation was affected by methyl lithium and only a 50% conversion was achieved. Linear up to 200 ng.	Pb	283.3	5 ng	188 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	(150 ml min^{-1}) by placing the column in a toaster (cf. 187) at T = 235°C.	dithiocarbamate complex.					188
Electrothermally heated quartz tube (see ref. 187).	1.8m x 6mm glass column, 3% OV-1 on Chromosorb W, 80/100 mesh. N_2 = 65ml min^{-1} T_I = 180°C T_c = 90°C then 20°Cmin^{-1} up to 190°C T_{in} = 165°C	Organotin compounds, Me_nSn-Bu_{4-n} in water.	Tin compounds were extracted with a 0.1% tropolone in benzene solution from spiked water samples. Linear up to 33 ng.	Sn	224.6	0.1 ng	206

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
Flame and a flame heated ceramic tube.	1.5m x 4mm glass column, 5% Carbowax 20M on Chromosorb 750, 80/100 mesh, $T_c = T_I = T_{in} =$ 159-175°C.	Tetraalkyllead compounds.	Various atom cells developed, and simplex optimized.	Pb	283.3	17 pg Pb for most sensitive atom cell.	171
Mo furnace surrounded by an alumina sleeve, heated at 250K-s^{-1} to 2473K.	247mm x 1.22mm i.d. Mo column with a wall thickness of 0.81mm. Carrier gas of either: Ar at 44.7±	Na, Cu, Mn, Mg in inorganic salts.	Ar(3.8 L min^{-1}) and H_2 (1.2 l min^{-1}) used to provide an air free atmosphere around tube.	Na Cu Mn Mg			203 contd

Atomizer	Chromatogr.	Matrix	Comments	Element	Wavelength	Detection	Ref.
	2.1 μl s^{-1} or Ar + H_2 at 35.1 $\pm$0.8 μl s^{-1} and 13.5$\pm$0.4 μl s^{-1} respectively. T_c = 2093K.						203

2.2.2.3 Atomic Fluorescence Spectroscopy

Of the six types of atomic fluorescence in flames which have been observed (207, 208), the most widely used analytically has been resonance fluorescence. Direct line fluorescence has been found useful since the emission wavelength is different from the excitation wavelength thus enabling the effect of scattered radiation to be eliminated. Whilst continuum and laser sources have been used, chromatographic applications have utilized only line sources. It can be shown for such sources (207, 208) that fluorescence intensity, I_F, is directly proportional to source intensity, I_S, and to analyte concentration, when self absorption does not occur. As I_F depends on I_S, a stable, intense sharp line source greatly enhances sensitivity.

To this end vapour discharge lamps, microwave excited discharge lamps and pulsed hollow cathodes have been utilized. The flame used as the atom cell effects the fluorescence power yield by non-radiative loss of energy, or quenching. Quenching increases with temperature, as the number of collisions increases, and with increased quenching cross-section of the colliding particle, for example, argon has negligible quenching cross-section, hydrogen a low one, whereas oxygen has a large one. The flames used reflect these properties, the argon/hydrogen diffusion flame has been used but the temperature of this flame is insufficient to prevent chemical interferences. Thus the argon separated air/acetylene flame has been most widely used, except where atomization requirements make it essential to use the nitrous oxide/acetylene flame, again argon separated. In all cases a circular flame is the preferred geometry. Van Loon (209)

Table 5 Coupled Gas Chromatography - Atomic Fluorescence Spectroscopy

Detector	Chromatography	Matrix	Comments	Element	Ref.
Circular N_2 shielded circular Air/C_2H_2 flame.	See Table 4, ref. 193	Tetraalkyllead compounds.	FAFS 3 x more sensitive than FAAS, however, Electrothermal AFS was no better than electrothermal AAS.	Pb	
Electrothermally heated quartz tube furnace.					
Graphite cup furnace at 1000°C					193

first suggested the possible use of non-dispersive AFS as a detector for chromatography, noting its multi-element capability, ability for low level detection and simplicity of usage. This latter point is debatable, but a likely reason for the dearth of published GC-AFS results is the lack of sufficiently intense, stable and simple light sources. Van Loon's group in Toronto have published the only GC-AFS work (193), in which they used a nitrogen separated circular air/-acetylene flame, an inert gas shielded electrothermally heated quartz tube and a modified graphite cup atomizer. In the lead specific detection of tetraalkyllead compounds flame AFS proved a factor of three more sensitive than FAAS; however, no increase in detectability was found using AFS over AAS when the graphite cup or quartz tube atomizers were used. The availability of a commercial AFS instrument should increase the usage of the technique since the advantages of multi-element analysis and sensitive detection make AFS an excellent method for the determination of metals.

2.3 Conclusion

Historically, the MIP has proved the most popular of excitation sources for coupling with gas chromatography. This probably reflects its ability to monitor certain non-metallic elements as well as metals. Particular mention must be made of the ability to monitor halogens in the helium MIP. The only commercially available GC-MIP system unfortunately uses a low pressure plasma and thus has the attendant problems of vacuum lines and gas transfer from atmospheric pressure in the chromatograph to low pressure in the detector. The availability of the Beenakker TM_{010} cavity, which allows an atmospheric He plasma

to be sustained may yield a more satisfactory GC-MIP coupling.

All the plasma emission detectors offer a multi-element facility and long linear ranges which are their most attractive features as GC detectors. Unfortunately the ICP, and to a lesser extent the DCP, involve high capital investment and high running cost, and coupling of these detectors to GC may not prove cost-effective for all but the largest laboratories.

Atomic absorption detectors, whilst having short working ranges, offer adequate sensitivity for trace metal speciation work, especially if electrothermal atomization is used. Flame atomizers do not normally offer such a low level detection capability but give simplicity of design and the instrumentation is readily available in the majority of laboratories concerned with the analysis of metals. The development of simple, sensitive atom cells for coupled GC-FAAS is discussed in Chapter 4.

The drawback of any GC coupling is that only volatile organometallic species and volatile metal derivatives are separable. For the separation of non-volatile metallic species, liquid chromatography (LC) must be used. Thus the coupling of LC with atomic spectroscopy is proving an important field of interest.

3. A REVIEW OF COUPLED LIQUID CHROMATOGRAPHY - ATOMIC SPECTROSCOPY

3.1 INTRODUCTION

In considering GC the potential analytes had to be limited to either volatile organometallic species or volatile metal chelates. The use of liquid chromatography (LC) considerably expands the type of chemical and physical species which may be studied. The separation of ions, involatile high molar mass organometallic species in addition to volatile species, is possible using one or other of the popular LC configurations. Adsorption, ion-exchange, normal and reverse phase chromatography have all been used in conjunction with atomic spectroscopy.

3.2 CHOICE OF ATOMIC SPECTROSCOPIC TECHNIQUE

The coupling of LC with atomic spectroscopy has been reviewed (60, 156-158, 160) and has the added complication that the mobile phase is a liquid. Thus the atom cells, i.e. flame, furnace or plasma, must be capable of handling solvent flows, typically 0.1-4.0 $ml.min^{-1}$, which may be aqueous or organic in nature.

3.2.1 Flame Atomic Absorption Spectroscopy

In addition to offering excellent inter metal selectivity, flame atomic absorption has the advantage that it readily accepts liquid samples. In a study of the effect of various mobile phases on nebulization efficiency, Jones et al. (129) found that with methanol, ethanol, chloroform and benzene, 100% nebulization efficiencies could be

achieved at flow-rates of 1 $ml.min^{-1}$ whereas for water at the same flow-rate only 32% was nebulized into the flame. The use of organic mobile phases requires some modification of air/fuel ratios since the organic eluent can act as a secondary fuel. Koropchak and Coleman (210) found that operating a nebulizer at a slight backpressure not only negated the use of a post column diluter to match LC flow-rate with nebulizer uptake rate, but also gave improved signal to noise ratios with a standard nebulizer arrangement. The various LC-FAAS couplings reported in the literature are surveyed in Table 6.

The group at Kyushu University, Japan, utilized the sensitivity and selectivity of AAS to monitor Mg and K in chloride solutions after separation (211). They used a 'T' piece with one end placed in a water reservoir to balance LC and aspiration flow-rates. This group (211, 213) also utlized the same coupling to study the formation of various phosphates from ortho-phosphate up to Kurrol's salt, $(KPO_3)_n$. The group in Columbia, Missouri, used Cu specific detection to monitor EDTA and NTA concentrations by passing the column eluent into the nebulizer of the spectrometer (214) in mixed solutions and also in spiked sewage effluents (215). They expanded the range of amino carboxylic acid-copper chelates which could be monitored (216) to include EGTA and CDTA. The same group demonstrated that organic mobile phases, toluene/pyridine, could be used with the separation of various chromium chelates (217). Botre et al. (58), along with Messman and Rains (219), used the separation of tetraalkyllead compounds in petrol to demonstrate LC-FAAS couplings using organic mobile phases. The comment must be made that the extensive study of GC-AAS systems for the speciation of tetraalkyllead compounds has yielded more sensitive and rapid

analysis, Table 4 (GC-AAS).

Van Loon et al. (191) used direct coupling of the column eluent to the nebulizer to monitor copper amino acid complexes used in the treatment of metal poisoning and also to study zinc aryl and alkyl compounds in lubricating oils. Kahn and Van Loon (220) used a similar coupling to preconcentrate and speciate Au and Pt complexes from aqueous solutions.

Slavin and Schmidt (221), in their LC-FAAS coupling, operated the nebulizer in a starved mode by using an injection cup (222) for the determination of amino-acids after metal labelling. The concept of metal labelling of species to enable determination by atomic spectroscopy has great potential; however, the low sensitivity of flame AAS would be problematic for the analysis of amino-acids in body fluids at the levels they occur. A flow injection sample manipulator (FISM) was used by Renoe et al. (223) as an interface between the chromatograph and spectrometer. This FISM allowed the addition of matrix modifiers, in this case HCl/La_2O_3, to the HPLC eluent prior to introduction to the nebulizer of the spectrometer.

The majority of the LC-FAAS applications (Table 6) suffer from the problem of low sensitivity; indeed, very few of the published reports mention detection limits. The couplings do, however, offer real time monitoring of chromatographic peaks which is an advantage over the couplings to electrothermal atomizers.

3.2.2 Electrothermal Atomization - Atomic Absorption Spectroscopy

Electrothermal atomization, mainly using graphite furnaces, offers the advantage of high sensitivity for a single atomization; however, the necessity to dry and ash a sample prior to atomization makes it practically impossible to directly couple the eluent from a chromatograph to a furnace. Thus various indirect couplings have been used to overcome this problem.

Brinckman's group, at the National Bureau of Standards, developed two such indirect couplings (224). The first utilized a Teflon flow through cell from which the eluent was periodically sampled and injected into a graphite furnace, so called pulsed mode operation. In the second, termed survey mode, the eluent was collected by an autosampler and each collected fraction analysed by GF-AAS. These two sampling modes were demonstrated for the speciation of various Sn, Hg, As and Pb compounds (224); the detection limits quoted were not evaluated by any conventional method and should therefore be treated with care. The survey mode of operation was also used for the speciation of organometallic polymers and organo-tin silicates by the same group (225).

Koizumi et al. (226) used a HPLC-Zeeman GFAAS for the speciation of tetraalkyllead compounds in gasoline. The eluent was sampled every 250 µl whilst the flow was stopped and the sample vaporised in a high temperature furnace. The interference caused by background absorption was avoided by using Zeeman effect background correction. Vickrey's group also used Zeeman effect background correction in their couplings (227-229). They described an interface device which consisted of a

sampling valve, timing circuit and automatic coanalyte addition, in this case nickel ions (227) for selenium speciation. This interface was later microprocessor controlled (229) and 37 µl samples injected into the furnace from each 100 or 220 µl of eluent. They also used stream splitting of chromatographic peaks (228) prior to atomization for the speciation of tetraphenyllead and pulsed mode operation for the speciation of Cr (III) and Cr (VI) (228), where the eluent was sampled every 30 or 120 seconds. The coupling was also used for tetraalkyllead (230) and organo-tin speciation (230). With the former, the addition of iodine prior to atomization was found to enhance both the signal and precision. A similar effect was found by using zirconium coated cuvettes in the speciation of organo-tin compounds (230). Irgolic's group at the same institution used a similar automated interface for the speciation of arsenobetaine, arsenocholine and inorganic arsenic at the micro-gram level (231). In a joint study, Brinckman's and Irgolic's groups (232) demonstrated various chromatographic separations for the speciation of arsenic compounds in soil and water samples. The extremely high background molecular absorption levels encountered when ion pair reagents, such as THAN, were used, required Zeeman effect background correction, since normal deuterium arc correction proved insufficient.

Workers at the U. S. Department of Agriculture (218, 233) utilized a flow-through Teflon sampling cup as an interface between a low-capacity anion exchange column and graphite furnace. They speciated organic and inorganic reducible forms of arsenic in pesticide residues. They gave thorough details of a clean up procedure for use in the analysis of soil arsenical residues by the same procedure (233). This

flow through Teflon sampling cup is now commercially available and a data sheet is available on its application to arsenic speciation studies (234).

Another indirect form of coupling was utilized by Burns and coworkers (59) and Ricci et al. (235), namely hydride generation prior to atomization. In their comprehensive study of organotin compounds, the former group (59) found a thousand-fold increase in response to tin by using hydride generation followed by ETA as opposed to coupling the eluent directly to the nebulizer for flame atomization. The speciation of reducible forms of arsenic was achieved by Ricci et al. (235), using hydride generation prior to atomization by a heated quartz tube. The use of hydride generation circumvents the problems of low nebulization efficiency normally encountered with FAAS, thus enabling sensitive detection along with "real time" detection.

Table 6. Coupled Chromatography - Atomic Absorption Spectroscopy

Detector	Chromatography	Matrix	Comments	Element (Wavelength/ nm)	Reference
Flame AAS. The column is connected to the nebulizer and the venturi effect pulls the eluent through the column.	Chelex ion exchange resin, 100/120 mesh, packed into a 1 ml. syringe, resin volume 0.5 ml. 0.1-0.5 ml samples. Resin washed with 0.1M $CuCl_2$ to generate Cu form.	Solutions of EDTA and NTA; pH 4 - 9.	Chelates strip Cu from the column which is monitored by AAS, Cu signed then related to chelate concentration. Linear up to 50 x 10^{-6} mM EDTA or NTA.	Cu	214
Flame AAS with column connected directly to nebulizer.	60 cm x 1.0 cm i.d. Sephadex G-15 column. Eluent: 0.1M NaCl or 0.1M NaCl + 0.001M EDTA. 1 ml. sample	Detection of Mg and K in $MgCl_2$/KCl solution.	To balance column flow with aspiration rate, a 'T' piece used with third arm placed in water reservoir.	Mg K	211 contd

Detector	Chromatography	Matrix	Comments	Element	Ref.
	volume.		Linear from 10^{-5} – 1.7 x 10^{-4} M.		211
Flame AAS directly coupled through the nebulizer by Teflon tubing (0.023" i.d.)	60 cm x 2 mm i.d. Porasil A column, Eluent 0.5% (v/v) pyridine in toluene. Sample volume = 10µl.	Cr as the $Cr(acac)_3$, $Cr(HAP)_3$ and $Cr(HFAA)_3$ chelates.	Adjustment of oxidant and fuel flows were made to accomodate the solvent in the flame. Detection limit of 40 ng.	Cr	217
Flame AAS, see ref. 211.	94.5 cm x 1.5 cm Sephadex G-25 column. NH_4, H_2O/NH_4Cl (pH 10) eluent 0.02M, at 1.83 $ml.min^{-1}$. column preequilibrated with $MgCl_2$ solution.	Determination of various condensed phosphates by on column complexation with Mg.	Phosphates elute in order tetra, tri, di, mono, with free magnesium eluting last after 73 min. $W_{\frac{1}{2}}$ = 5 min. Linear up to 20 µg phosphate as triphosphate.	Mg (285.2)	212

Detector	Chromatography	Matrix	Comments	Element	Ref.
Flame AAS, direct coupling through nebulizer. Flow spoiler removed from chamber, ca. 80% of eluent reaching flame.	50 cm x 2.6 mm. i.d. ODS column. $T_c = 50^{o}C$ Eluent, 3:2 v/v H_2O/MeOH at 1.0 $ml.min^{-1}$, at 1200 psi, 1 µl sample.	Tetraalkyllead compounds in petrol.	No background problems found possibly due to the large and constant amount of MeOH in eluent. Linear from 0.25 to 50 µg.	Pb	58
Flame AAS, direct coupling, cf. ref. 217. Air/C_2H_2 flame.	5 cm x 2.1 mm i.d. Aminex A-14 resin, 4% cross linked with SDVB, 20 ± 3 µm. 0.05M$(NH_4)_2SO_4$ eluent at 2.0 $ml.min^{-1}$.	Separation of $Cu_2(EGTA)$, $Cu(NTA)^-$, $Cu(EDTA)^{2-}$ and $Cu(CDTA)^{2-}$.	pH of sample affects formation of $Cu_2(EGTA)$ but not of other complexes. Detection limits/ng Cu of EGTA = 13.5 NTA = 16.2 EDTA = 29.4 CDTA = 450 in order of elution.	Cu	216

Detector	Chromatography	Matrix	Comments	Element	Ref.
Flame AAS, direct coupling through nebulizer see ref. 216.	Identical to ref. 216.	Copper chelates of aminocarboxylate ions in spiked sewage effluents.	Assumptions made as to detection limits and hence feasibility of method. Detection limits/ng Cu NTA = 10.7 EDTA = 23.6	Cu	215
GFAAS, hplc eluent passed into a sample well then sampled, 10-50 µl, into a standard furnace. Program Dry - 80°C 15s Atomize - 2700°C 5s	250 x 4.6 mm columns. Lichrosorb C_{18} RP on 10 µm silica, Eluent MeOH at 0.12 $ml.min^{-1}$	Triphenylarsine.	Coupling operated in either a pulsed mode, where the eluent was passed into a Teflon flow through cup periodically sampled, or in a survey mode where the eluent was collected by an auto-	As (193.3)	224 contd.

Detector	Chromatography	Matrix	Comments	Element	Ref.
Dry - 100°C 10s Char - 100°C 10s Atomize - 2500°C 15s	Lichrosorb C_2 RP 1.5 ml.min^{-1} of MeOH.	Ph_3SnCl, Pr_3SnCl, Bu_3SnCl.	sampler and each fraction analysed.	Sn (224.6)	
Dry - 80°C 25s Atomize - 750°C 12s	Lichrosorb C_8 RP Eluent a) 0.01M NH_4OAC b) 25ppm mercaptoethanol in MeOH. Flow a + b (96 + 4) for 25 min then gradient, 10% min^{-1}, to 100% b at 0.30 ml.min^{-1}.	MeHgCl, EtHgCl, PhHgCl, ^{n}PrHgCl, in 1 + 1 H_2O/-MeOH.		Hg (253.7)	
Dry - 25°C 20s Char - 80°C 10s Atomize - 2000°C 10s	Lichrosorb Si-100 10 µm silica, eluent - hexane/CH_2Cl_2 (95 + 5) 0.33 ml.min^{-1}.	Ph_6Pb_2		Pb (283.3)	224

Detector	Chromatography	Matrix	Comments	Element	Ref.
Flame AAS, column coupled directly to nebulizer. Air/C_2H_2 flame.	Partisil-10 SC X cation cation exchange column $T_c = 55^{\circ}C$ 1M NH_4NO_3 at 4.0 ml-min^{-1} as eluent 25µl sample size.	Separation of Cu EDTA. Cu-trien, Cu-glycene. complexes.	Use of UV/Vis detection enabled only Cu-trien to be monitored, with reduced sensitivity compared to AAS.	Cu	
	25 cm ODS-SILXI column. Eluent: 50-100% methanol/water gradient in 10 min.	Alkyl and aryl Zn additives in lubricating oils samples diluted in CH_2Cl_2.	AA detector shown superior to UV/Vis detection.	Zn (213.9)	191
Flame AAS. Use of column directly coupled to nebulizer. Aspiration rate controls flow of eluent	Basic anion exchange Dowex 2X-8 column soaked overnight in 3M HCl followed by water rinsing.	Pt and Au in aqueous solutions.	The Pt and Au solutions (pH 6) passed through the column, the metals retained and then eluted with	Au Pt	220 contd

Detector	Chromatography	Matrix	Comments	Element	Ref.
through column.	Pt and Au complexes eluted with NH_4OH (75%).		NH_4OH into nebulizer. Linear from 2 to 10µg for Au and from 35-175 µg for Pt.		220
GFAAS using Zeeman background correction. Dry - 100°C 25s Ash - 1000°C 1s Atomize - 3000°C 5s using $NiNO_3$ as co-analyte and Ar shield gas (4 $l.min^{-1}$) 37µl injections.	10 m, Partisil-PXS-ODS column. Eluent: $MeOH/H_2O$ (2 + 1) at 0.3 $ml.min^{-1}$ 20µl injection.	Se specific detection of $Me_2NC(Se)NH_2$ and $(C_6H_5CH_2)_2Se$.	Design and operation of interfacing device consisting of sampling valve, timing circuit and coanalyte addition described. Linear from 10 to 100 ppb for a single atomization.	Se (196)	227

Detector	Chromatography	Matrix	Comments	Element	Ref.
Flame AAS; see refs 211, 212 for interface.	97.5 x 1.5 cm i.d., Sephadex G25 column.	Monitoring of Kurrol's $(KPO_3)_n$, di-, tri-, and ortho-phosphate as Mg complexes.	Kurrol's salt used as useful marker for void volume of column Estimation of stability constants also made.	Mg (285.2)	213
GFAAS, Dry - 100°C 20s Char - 700°C 30s Atomize - 2500°C 10s	8 cm Bio-Rex 70, weak acidic cation exchange resin.	Cu-amino acid complexes in human serum	The eluent from the column collected by an autosampler and then automatically injected into furnace.	Cu (324.7)	
	24 cm, silica gel (100/120 mesh, ASTM D1314 - 61T, grade 923) Flow rate = 0.40 ml.min^{-1} acetone/water (60+40), pH 7-8.	Naturally occurring Cu-amino acids, Cu-histidine and Cu-glutamine from an aqueous mixture.			236

Detector	Chromatography	Matrix	Comments	Element	Ref.
GFAAS using Zeeman effect background correction.	500 x 2.5 mm column, Hitachi Gel No. 3010. Eluent: MeOH at 0.67 $ml.min^{-1}$.	Tetraalkyllead compounds in petrol.	10 µl samples from each 250 µl of eluent injected into furnace.	Pb (283.3)	226
GFAAS using autosampler as interface, see ref. 224. T_{at} = 2700°C	300 x 7.8 mm column, SDVB copolymer (10µm) Eluent: THF at 1 $ml-min^{-1}$ or THF/CH_3CN (19 + 1).	SEC used for organometallic polymers, OMP-1, OMP-2, OMP-4.	A 50s interval exists between injections, thus at 1 $ml.min^{-1}$ only 2.4% of eluent sampled.	Sn (286.3)	
	Li Chrosorb C_{18} (10µm) 250 x 3.2 mm column, Eluent: ethanol at 0.25 $ml.min^{-1}$.	RPC used for organotin silicates.	Linear up to 20 ng Sn or Si for a 20µl injection	Si (251.6)	225

Detector	Chromatography	Matrix	Comments	Element	Ref.
Flame AAS using standard flame conditions eluent passed into nebulizer.	25 x 0.46 cm Partisil-10 SCX column. Eluent, NH_4NO_3 at various molarity and pH, 1 to 2 $ml.min^{-1}$.	Use of metal labelling to determine amino-acids, in this case histidine as copper complex.	Nebulizer operated in starved mode by use of injection cup (see ref. 222). 100 µl drops from column into cup. Detection limit of 48.5 ng.	Cu	221
GFAAS using Zeeman effect background correction. Automated interface which controls eluent sampling, coanalyte addition, injection and furnace operation.	µ - Bondapak (C_{18}) RPC column. Eluent: H_2O/acetonitrile/acetic acid and 0.005M heptane-sulphonic acid (95/5/6).	Separation of arsenobetaine, arsenocholine and inorganic arsenic.	Chromatograms illustrating separation of arsenic compounds at 1 µg level given.	As	231

Detector	Chromatography	Matrix	Comments	Element	Ref.
GFAAS with microprocessor controlled interface, details of interface and computer control program given.	Partisil SCX cation exchange column. Eluent: 0.1F acetate buffer (pH 4.3).	Separation of Cr(III) and Cr(VI).	Pulsed mode operation, eluent sampled for GFAAS only every 30 to 120s.	Cr	
Dry - 60°C 20s Ash - 250°C 12s Atomize - 2400°C 5s	Lichrosorb C_{18} (10μm) Eluent: MeOH/H_2O (90/10) at 0.5 ml-min^{-1} 20 μl injection.	Tetraphenyllead	Total consumption mode, peak containing eluent stream is stored prior to GFAAS analysis.	Pb (283.3)	228
GFAAS using Zeeman effect background correction. Dry - 60°C 25s Ash - 500°C 12s Atomization - 2400°C 5s	25 cm Lichrosphere (10 μm) RPC column. Eluent: MeOH/H_2O (90/10).	Tetraphenyllead.	Eluent stream containing lead compound is stored, after separation, in tubing (10'x 0.05 cm) prior to injection into furnace.	Pb (283.3)	229 contd

Detector	Chromatography	Matrix	Comments	Element	Ref.
Microprocessor controlled interface, see ref. 228. 37 µl injection from each 100 µl or 220 µl sample of eluent.			Detection limit of 480 pg.		229
GFAAS, 20 µl injections every 45s. Dry - 150°C 15s and 200°C 5s Atomize - 2700°C 10s No background correction.	25 cm x 3.2 mm i.d. Lichrosorb SAX (10 m) column. Eluent: 0.05M NaH_2PO_4 at 0.5 $ml.min^{-1}$.	Speciation of DMA, MMA and arsenilic acid.	The HPLC separation schemes were employed for As speciation work with several soil and drinking water samples. Linear from 0.1 to 10ng As.	As (193.7)	
	Same column but with 0.03M ammonium acetate/0.045M acetic acid	Speciation of MMA, DMA and As(III).			232 contd

Detector	Chromatography	Matrix	Comments	Element	Ref.
	Eluent at 0.25 ml.min^{-1}				
No background correction.	25 cm x 3.2 mm i.d. Altex SCX column (10μm) with 0.0375M ammonium acetate/ acetic acid.	Speciation of As(III) and As(V).			
Zeeman effect background correction.	Eluent at 0.15 ml.min^{-1} 30 cm x 4 mm i.d., μ-Bondepak C_{18} RPC (10μm) column, H_2O/-MeOH (95/5) 0.005M w.r.t.TBA, at ph 7.3 adjusted with phosphoric acid.	Speciation of As(III) and As(V).	The use of the ion-pair reagents THAN or TBAP requires the superior background correction afforded by the Zeeman effect. Linear up to 500 ng As.		
Zeeman effect background correction.	25 cm x 4.6 mm i.d., Altex Chromosorb RP-18	Speciation of As(III), DMA, MMA and As(V).			232 contd.

Detector	Chromatography	Matrix	Comments	Element	Ref.
	column (10 μ m). H_2O/-MeOH saturated with THAN for 23 min then MeOH, at 1.0 ml min^{-1}.				232
GFAAS, using Teflon flow through sampling cup as interface. 20 μl injections at 43s intervals. Dry - 110°C 8s Char - 1200°C 7s Atomize - 2500°C 8s 20s furnace cooling period.	25 cm x 3 mm i.d., low capacity anion exchange column (Dionex) gradient elution from H_2O/MeOH (80 + 20) to 0.02M $(NH_4)_2CO_3$-MeOH (85 + 15) at 1.2 ml-min^{-1}. 5-25 μ l injections. 8-12 min equilibration time.	Separation of DMA, MMA, As(III), and As(V).	The column packing prepared by passing a suspension of a high capacity strong anion exchange latex over a cation exchange resin Linear from 5 to 200ng As.	As (193.7)	218

Detector	Chromatography	Matrix	Comments	Element	Ref.
GFAAS, see ref. 218.	HPLC column and conditions same as ref. 218.	Arsenical residues, DMA, MMA, As(III) and As(V) in soils.	Extraction and extensive cleanup procedure is given.	As (193.7)	233
GFAAS using Zeeman effect background correction. Dry - 80°C 20s Ash - 370°C 10s Atomize - 2300°C 5s	25 cm Lichrosorb 10 µm C-18 ODS column Eluent 0.5 $ml.min^{-1}$ 80:20 MeOH/H_2O for 28 min followed by a step gradient to 100% MeOH.	Tetraalkyllead compounds.	Addition of Iodine found to enhance signal and precision.	Pb	
Dry - 80°C 20s Ash - 400°C 10s Atomize - 2300°C 5s	Same column, eluent: MeOH/H_2O (97.5 + 2.5) isocratic at 0.1 $ml-min^{-1}$.	Organotin compounds.	Increased signal and precision found when Zr coated graphite cuvettes were used.	Sn (224.6)	230

Detector	Chromatography	Matrix	Comments	Element	Ref.
Flame AAS using N_2O/C_2H_2. Directly coupled through nebulizer or hydride generation followed by electrothermal, quartz furnace, AAS.	250 x 3.0 mm i.d., ODS Spherisorb S5W $T_c = 23 \pm 0.1^{\circ}C$, Eluent: acetone/pentane (3 + 2) at 1.0 ml-min^{-1} for methyltin compounds; acetone/pentane (7 + 3) at 1.2 $ml.min^{-1}$ for ethyl tin compounds.	Methyl and ethyl tin compounds both SnR_4 and $SnR_{4-n}Cl_n$.	The design of a miniature, continuous flow hydride generation system given. Linear up to 50 µg using flame and up to 100ng for hydride generation.	Sn (286.3)	59
GFAAS, 10-100 µl injections.	35 x 1 cm i.d. column, 9 cm AG50 W-X8 (100/120 mesh) cation exchange resin, 26 cm AG1-X8 (100/120 mesh) anion exchange resin.	As(III), As(V), MMA, and DMA in arsenic contaminated, sediment interstitial water, up to 2 ml injected.	The separated As species were collected in fractions from which injections were made into furnace.	As	237 contd

Detector	Chromatography	Matrix	Comments	Element	Ref.
	Column conditioned with 50 µg of each arsenic species.		Detection limit 10ppb in original sample.		237
AAS, using air/C_2H_2 flame directly coupled through nebulizer.	300 mm x 3.9 mm i.d., µBondapak C_{18} column, Eluent: acetonitrile/water (70 + 30) at 3.0 ml.min^{-1}. 20 µl injections.	Tetraalkyllead compounds in petrol.	The relative merits of UV and AAS detection discussed with latter proving more suitable for this application. Linear from 1.1→11 µg	Pb (283.3)	219
Flame AAS using flow injection sample manipulator (FISM) interface with fuel rich air/C_2H_2 flame.	100 mm x 7.5 mm i.d., Spheregel TSK 2000SW (10 µm). Eluent: 130 mmol NaCl, 6.8mmol NaOH, 3mmol NaN_3, 4mmol KCl and 10mmol TES at 0.4 ml.min^{-1}, pH = 7.43 at 37°C	Study of metal ligand binding in clinical samples.	FISM interface described enabled La/HCl to be mixed with eluent prior to introduction through nebulizer. Linear up to 3.75 mmol Ca.	Ca (422.7) Mg (285.2)	223

Detector	Chromatography	Matrix	Comments	Element	Ref.
AAS using hydride generation and electrothermal, quartz tube, atomization. $T = 800^{\circ}C$.	3 x 500 mm standard Dionex anion column, Eluent: 2.6 $ml.min^{-1}$. $0.0024M\ NaHCO_3$/ $0.0019M\ Na_2CO_3$/ $0.001M\ Na_2B_4O_7$.	Speciation of As(V), MMA, p-APA.	Miniature hydride generation system, see ref. 238. 1 hour reequilibration time between eluent systems. Detection limit of 10 $ng.ml^{-1}$.	As (193.7)	
	$0.005M\ Na_2B_4O_7$.	Speciation of As(III) and DMA.			235
GFAAS using a fraction collector as interface. Dry - $100^{\circ}C$ 30s Char - $1300^{\circ}C$ 30s Atomise - $2700^{\circ}C$ 10s 20 µl injections.	25 cm x 2.6 mm., ODS-HC Sil-X-1. Eluent: either gradient from 50% MeOH to 100% MeOH in 25 min. or 20% MeOH for 10 min then gradient to 100% in 30 min.	Organophosphorus compounds in lubricating oil.	The chromatographic analysis time = 25 to 40 min, whereas GFAAS analysis time = 100-120 min. Detection limit of 0.3 $mg.l^{-1}$.	P (213.6)	

Detector	Chromatography	Matrix	Comments	Element	Ref.
GFAAS, see refs. 224, 231, 232.	See ref. 218.	Inorganic and organo-arsenic compounds in oil shale retort and process waters.	Compounds found were: arsenite, arsonate, methylarsonic acid, phenylarsonic acid, along with one unidentified compound.	As (193.7)	239
GFAAS using fraction collector as interface with manual injections.	Anion exchange resin Dowex 1-X4, 200/400 mesh in acetate form, 115 mm x 10 mm, Eluent: 0.1% acetic acid 65 min, 5% acetic acid 130 min then 1M HCl for 65 min. Flow rate = 20 drops min^{-1}.	Separation of DMA, MMA and As(III)/As(V) As(III) levels found separately in soil polluted with As.	Extraction procedure given for soils. The chromatographic separation does not speciate As(III) and As(V).	As (193.7)	240

Detector	Chromatography	Matrix	Comments	Element	Ref.
AAS using fraction collector as interface.	33 x 1.0 cm Sephadex G15 column. Eluent: 0.2M $NaClO_4$ (pH 2). at 40 $ml.hr^{-1}$. 46 x 1.0 cm Sephadex G-10, eluent 0.1M $HClO_4$ at 19 $ml.hr^{-1}$.	Separation of successive Cr(III) isothiocyanato complexes. with SCN/Cr ratio of 1→6.		Cr	241

3.2.3 Flame Atomic Fluorescence Spectroscopy

The advantages of AFS as a chromatographic detector have been extolled by Van Loon (205) as simultaneous multi-element detection with greater sensitivity than AAS. Such detectors have been utilised a little more with LC, Table 7, than with GC. Van Loon's own group have used non-dispersive simultaneous multi-element FAFS for the speciation of Cr(III), Ag(I), Mn(II) and Mn(VII) in synthetic sea water (242). Excellent resolution was demonstrated for a mixed solution (10 mg l^{-1} of each species, 10 ml injection); however, the high sensitivity of AFS was not tested. This group also demonstrated the multi-element capability of coupled LC-FAFS for the speciation of Cu, Ni and Zn amino-acid and amino-carboxylic acids (243). Unfortunately no mention of the metal concentrations was made.

Siemer and co-workers (244) reported the use of continuum source FAFS in the study of the acetylation reaction of ferrocene by acetic anhydride. They found it much easier to follow the reaction by Fe specific detection than by conventional UV detection. Mackey (245) in a study of the interactions of simple cations, Cu, Fe and Zn, with macroreticular resins used multichannel FAFS but quantified the results by batch measurements using graphite furnace AAS. The LC-FAFS system was found to be linear up to 1.0, 1.6 and 0.6 mg l^{-1} for Cu, Fe and Zn respectively, deviation from linearity was said to occur at 20 times the detection limit as defined by Larkins (246).

Table 7 - Coupled Liquid Chromatography - Flame Atomic Fluorescence Spectroscopy

Detector	Chromatography	Matrix	Comments	Element	Ref.
FAFS using a N_2 shielded circular air/ C_2H_2 flame, eluent passed directly into nebulizer.	10 cm x 1 cm column, 80 mesh Chelex 100 washed with HCl (40 ml) and water (40 ml) at 1 ml min^{-1}. Eluent: H_2O (pH 6) for 4 min then 2M HNO_3.	Speciation of Cr(III), Cr(VI), Ag(I), Mn(II), and Mn(VII). in standards and synthetic sea water.	In the sea water a scattering peak, due to NaCl, appears well before Cr(III), Mn(II) or Ag(I) elutes.	Cr Mn Ag	242
As above.	Partisil-10 SCX column at 55°C. Eluent: water until first peak eluted then a 5 min convex gradient to 100% 1M NH_4NO_3 at 4.0 ml min^{-1}	Separation of Cu, Ni, and Zn EDTA, Trien and glycine complexes.	The glycine and EDTA complexes have almost identical retention times, however multielement AFS gives excellent resolution.	Cu Ni Zn	243

Detector	Chromatography	Matrix	Comments	Element	Ref.
FAFS using air/C_2H_2 capillary tube burner, Ar shielded, Xe continuum lamp source, direct coupling to nebulizer.	50 cm x 2 mm chromosep S column packed with pellicular 10 µm silica gel. Eluent: diethylether/methanol (40/1) at 0.5-2.0ml.-min^{-1}.	Investigation of acetylation reaction of ferrocene by acetic anhydride.	Progress of reaction more specifically followed using AFS than normal UV detection.	Fe (248.3 and 252.2)	244
FAFS; see ref. 242.	6 mm column of XAD-2 resin. Various elution systems used.	Study of absorption of trace metals on amberlite resins.	Metals are not desorbed by MeOH but by methanolic HCl, methanolic NH_3 and Na_2H_2EDTA. Linear up to: 1 $mg.l^{-1}$ Cu, 1.6 $mg-l^{-1}$ Fe and 0.6 $mg.l^{-1}$ Zn.	Cu Fe Mg Zn	245

3.2.4 Atomic Emission Spectroscopy

The relatively low excitation temperature of the various atomic spectroscopic flames again limits their usefulness as atom cells for coupled LC-AES applications. Flames have been used in various configurations as molecular emission detectors; for example, McGuffin and Novotny (247) monitored HPO bands for phosphorus selective detection of various compounds eluting from a microbore LC column. Similarly Cope and Townshend (248) have used a phosphorus sensitive MECA detector as a detector for HPLC.

The low neutral gas temperature of the MIP makes it very sensitive to large solvent flow-rates. Although several workers have devised continuous nebulization systems (249-251) for the plasma, it has proved singularly unpopular in LC applications. By contrast, both the direct current and inductively coupled plasmas with their ability to withstand both organic and aqueous solvent flows have found various applications as LC detectors (60, 61).

3.2.4.1 Direct Current Plasma

Once again the group at Amherst, Massachusetts, have been the main exponents of coupled LC-DCP OES, Table 8, using both two and three electrode plasmas (61, 252-254). They found (253) that the standard nebulization arrangement was sufficient for eluents used in ion exchange and reverse phase chromatography but when used in conjunction with the organic solvents used for adsorption chromatography a rapid build-up of carbon resulted. Thus they designed a novel nebulizer which had an

efficiency of 20-25% and could be run continuously for up to ten hours with no carbon deposits forming. The couplings were used in the speciation of diethyldithiocarbamate complexes of Co, Cu, Ni (252), Hg and Cr(253). The study of mixed ligand complexes of the type $Cr(HFA)_n$-$(TFA)_{3-n}$, for n = 0, 1, 2, 3 (254), was aided by the metal specific detection afforded by the coupled system.

Koropchak and Coleman (255) used a cross flow nebulizer in their LC-DCP coupling. They studied nebulization parameters to optimize the plasma detection capabilities when interfaced to a liquid chromatograph. They demonstrated its capability in the speciation of three cadmium salts; however, the hope that the DCP could provide sensitive specific detection for the halogens was not realised.

Table 8. Coupled Liquid Chromatography - Direct Current Plasma Optical Emission Spectroscopy

Detector	Chromatography	Matrix	Comments	Element	Ref.
DCP, using spectraspan III instrument	250 x 4 mm i.d., 8 μm Spherisorb SEP. Eluent: 5:15:80 acetonitrile, diethylether and skelly B at 2.2 $ml.min^{-1}$. column washed prior to use with 0.5% pyridine in skelly B.	Separation of metal diethyldithiocarbamates.	DCP detector in series with UV detector used to confirm metal content of eluted peaks. Linear from 5 to 500 ng Co and from 10 to 500 ng Cu.	Co Ni Cu	252
DCP (Spectraspan III) For reverse phase and ion exchange chromatography, eluent passed directly into	250 mm Partisil ODS column. Eluent: H_2O/acetronitrile (60:40) at 0.65 $ml.min^{-1}$.	Speciation of: $Cu(enAA_2)$, $Cu(enTFA_2)$ and the Ni analogues.	Nebulization of eluents used for adsorption chromatography caused rapid C buildup and thus required a new	Cu (324.7) Ni (341.5)	253 contd.

Detector	Chromatography	Matrix	Comments	Element	Ref.
standard nebulizer system.	250 mm, 10 μm Partisil 10 silica. Eluent: 8% CH_2Cl_2 in skellysolve B.	$Cr(HFA)_3$ and various mixed ligand chelates formed by reaction of Cr with TFA and HFA.	design of nebulizer. Eluent was directed at chamber wall in a fine jet and resulting mist swept into plasma. Nebulization efficiency of 20-25% was attained with no C buildup over 10 hr period. Linear from 30 to 4000 ng Cu and from 60 ng to 2.5 μg Cr.	Cr (267.7)	
	250 mm, 8 μm Spherisorb, eluent: 5:20:75 acetonitrile/diethylether/skellysolve B.	$Hg(DEDTC)_2$, $Cr(DEDTC)_2$.		Hg (253.7) Cr (267.7)	253

Detector	Chromatography	Matrix	Comments	Element	Ref.
DCP plasma, same interface for hydrocarbon eluents as ref. 253.	300 x 4 mm i.d., 10 μm Partisil silica, eluent: 6% acetonitrile in CH_2Cl_2 1.5 $ml.min^{-1}$.	Speciation of: mer and fac isomers of $Co(BAA)_3$ and $Co(PAM)_3$.	Detection limit of 100 ng for Cr.	Cr (267.7)	
	8% CH_2Cl_2 in hexane.	Mixed ligand complexes of $Cr(HFA)_n(TFA)_{3-n}$ and the mer/fac isomers of $Cr(TFA)_3$.			
	Concave gradient of 3-20% CH_2Cl_2 in hexane.	As for above only better peak shape and shorter analysis time achieved.			254

Detector	Chromatography	Matrix	Comments	Element	Ref
DCP using crossflow nebulizer with direct introduction of eluent.	500 mm x 5 mm, Sephadex G-10 column. Eluent: H_2O at 2.0 $ml.min^{-1}$.	Separation of Cd; sulphate, bromide and acetate.	Examination of nebulization parameters concerned with coupling reported.	Cd (228.8)	255

3.2.4.2 Inductively Coupled Plasma

The coupling of LC with ICP-OES is normally directly through standard nebulizer arrangements. Browner and co-workers (256) considered the effect of nebulization chamber position using both Meinhard (257) and fixed crossflow (258) nebulizers for LC-ICP couplings. Although they only studied aqueous eluents, they found peak broadening and distortion occurred when the chamber was placed inside the ICP gas box due to extended liquid transport. If, however, the chamber is sited outside the gas box, then a loss in signal commensurate with aerosol transport over an equivalent distance occurred.

Fraley et al. (259. 260) built on their experience with hybrid techniques and compared FAAS and ICP-OES as HPLC detectors for the speciation of copper amino-carboxylic acid chelates (259). Both techniques were found to yield a similar response; however, the multi-element facility of ICP-OES was demonstrated using a dummy column to simulate chromatographic conditions. The simultaneous detection of Ca, Cu, Mg and Zn amino-carboxylic acid chelates with linearity up to 1 μg (260) illustrates another advantage of OES over AAS, i.e. long linear calibrations.

Gast et al. (261) demonstrated a coupling using a fixed crossflow nebulizer for the speciation of carbonyl complexes of Fe and Mo, various forms of As, dialkyl-mercury compounds, tetraalkyllead compounds and various ferrocene derivatives. The ICP-OES detector was evaluated by injecting small samples into the nebulizer. They studied the effect of solvent composition and determined both linear ranges

and detection limits by this method. Morita et al. (262) used direct sampling of eluent to the nebulizer for the estimation of Co/P/C ratios in vitamin B_{12} and also in the simultaneous multi-element detection of various proteins. Kurosawa et al. (263) used the same coupling to unequivocally identify the presence of arsenobetaine in shark liver and muscle.

Hausler and Taylor (264, 265) used ICP-OES in conjunction with size exclusion chromatography and evaluated a number of spray chamber designs. Using toluene as eluent (264) it was found that cooling the chamber to $0^{\circ}C$ resulted in better sensitivity being obtained. This evaluation, along with determination of detection limits, was carried out in the absence of the chromatographic column. When pyridine was used as eluent (265), best sensitivity was achieved with the chamber thermostated to $20^{\circ}C$. Detection limits, found by the same procedure as above, were slightly worse than those obtained with toluene. Gardner et al. (266) used ICP-OES in series with UV detection to monitor the speciation of Ca and Mg in natural water filtrates. If both detectors gave a response, the tenuous implication that the metal was organically bound was made.

This last example illustrates the main advantage of hybrid chromatographic techniques, i.e. they yield specific interpretation. The most definite conclusion from the chromatographic data (266) was that a species contained Ca, Mg, or neither, the rest was speculation. Thus, these hybrid techniques not only simplify chromatographic interpretation, but enable selective data to be obtained.

Table 9. Coupled Liquid Chromatography - Inductively Coupled Plasma Optical Emission Spectroscopy

Detector	Chromatography	Matrix	Comments	Element	Ref.
ICP, eluent from column passed directly into nebulizer. All Ar plasma. For FAAS work air/C_2H_2 flame used.	Aminex A-14 column; see ref. 216.	Separation of EDTA and NTA chelates.	Compared ICP with FAAS detection for Cu chelates and found both gave similar response. Also used dummy column to simulate chromatography for various metals.	Cu (324.7)	259
ICP all-Ar plasma, outlet of column connected by capillary Teflon tubing to nebulizer of cross-flow design.	250 x 4.6 mm i.d. Zorbax-C8 column, eluent: 70% (v/v) Eluent: 5 min. linear gradient of 50-55% ethanol then 5 min.	Separation of iron carbonyl complexes. Separation of various molybdenum carbonyl complexes.	ICP was tested as a HPLC detector by injecting small samples through an injector into the nebulizer, to evaluate effect	Fe (259.94) Mo (281.615)	261 contd

Detector	Chromatography	Matrix	Comments	Element	Ref.
	linear gradient up to 80% EtOH, 1 ml.min^{-1} 20 µl injection.		of various solvents; sensitivity; linearity and detection limits.		
	Hypersil (6 µm), 100 × 4.6 mm i.d., eluent: 30% MeOH, 1% (w/w) n-hexadecyltrimethylammonium bromide, 0.08M, pH 5, at 1.2 ml.min^{-1}.	Separation of DMA, MMA, p-APA, As(V), phenylarsonic acid.		As (278.022)	
	Eluent: EtOH - 0.05M NaBr (1:2) pH 3, 1.2 ml.min^{-1}.	Separation of Hg(II) methylmercury, ethylmercury and propylmercury.		Hg (253.652)	
	Eluent: 75% EtOH 1.4 ml.min^{-1}. 30 µl injection.	Tetraalkyllead compounds in petrol.		Pb (283.306)	261 contd

Detector	Chromatography	Matrix	Comments	Element	Ref.
	250 x 3 mm. i.d., silica Gel Si60 (8 μm), eluent: toluene 1.4 ml.min^{-1}.	Separation of various ferrocene compounds.		Fe (259.94)	261
All-Ar ICP, eluent passed directly into nebulizer.	600 x 2 mm, TSK GEL 3000 SW eluent: 0.9% NaCl, 1.0 ml.min^{-1}.	Separation of vitamin B_{12}. Separation of various proteins; ferritin, catalase, aldolase, albumin, cytochrome C, chymotrypsinogen A.	Multi-element detection used to calculate Co/P/C ratio. Simultaneous multi-element detection of Cu, Fe, Mn, P, Zn.	C (246.7) Co (228.6) Cu (324.9) Fe (259.9) Mn (257.6) P (241.9) Zn (213.8)	262

Detector	Chromatography	Matrix	Comments	Element	Ref.
All-Ar ICP, eluent passed directly into nebulizer.	Either: Nagel-Nucleosil 10-SA cation or 10-SB anion exchange resin. Eluent: 0.025M phosphate buffer, pH 7.4	Identification of arsenobetaine in shark muscle and liver by comparison with standard chromatogram of arsenobetaine, DMA, MMA, As(III) and As(V).	Arsenobetaine matched, on both resins, the main As compound found in the shark tissues.	As (193.7)	
ICP, all-Ar plasma, eluent passed directly to nebulizer; various spray chamber designs evaluated with and without cooling to 0°C.	100-A -Styragel waters column at a flow rate of 1.0 or 0.5 ml min^{-1} of toluene. Bio-Beads SX-2 size exclusion column; Eluent: toluene at	Separation of various Si, Pb, Sn and Ge organometallic compounds. Separation of a 21-element standard, metal salts of	The various spray chambers, and detection limits were evaluated without the chromatographic column being used. These detection levels are com-	Al, Ag, Ba Cd, Cu, Fe Mg, Mn, Ni Pb, Si, Sn Ti, V, Zn.	264 contd

Detector	Chromatography	Matrix	Comments	Element	Ref.
	same flow rates. 200 µl injected.	dialkylbenzene sulphonates, in an organic matrix.	parable to those found for aqueous solutions.		264
Ar ICP, see ref. 264. Spray chamber thermostated to 20°C.	100-A µ-Styragel waters column, eluent: pyridine at 0.5 or 1.0 ml-min^{-1} or toluene at same flow rate.	Separation of a 21-element standard (see ref. 264), ferrocene and derivatives, copper and cobalt complexes, and organically bound metals in solvent refined coal.	Detection limits in pyridine, determined by same method as 264, and are generally slightly worse than those found using toluene.	See ref. 264	265
Ar ICP, eluent taken from UV detector directly to crossflow	250 x 1.6 mm i.d., AGI X 4 (< 400 mesh) anion exchange resin	Separation of NTA and EDTA chelates of Cu, Zn, Ca and Mg.	The data acquisition storage and output is microprocessor	Cu Ca Mg	260 contd

Detector	Chromatography	Matrix	Comments	Element	Ref.
nebulizer. 32-element polychromator used for simultaneous detection, or monochromator for single channel operation.	Eluent: 0.05M $(NH_4)_2SO_4$.		controlled. Linear up to 1 μg for all elements.	Zn	260
Ar plasma; see ref. 259.	600 x 7.5 mm i.d., TSK 3000 SW size exclusion column, or a 500 x 7.5 mm i.d., TSK 2000 SW column. Eluent: H_2O at 1.0 or 1.5 $ml.min^{-1}$.	Speciation of dissolved Ca and Mg in natural water filtrates.	By using UV detection as well as ICPOES, inference as to the organic binding made.	Ca Mg	266

3.3 Conclusion

Atomic absorption, whilst being the most inherently metal specific of the atomic spectroscopic techniques, suffers from major drawbacks when coupled with liquid chromatographic eluents. In LC-FAAS with reverse phase, i.e. mainly aqueous, eluents the low nebulization efficiency limits the sensitivity of the technique. Operation of the nebulizer in a starved mode, for example by using an injection cup device, may slightly alleviate this problem. When normal phase, i.e. organic, eluents are used then higher nebulization efficiencies are possible; however, transport of large amounts of organic solvents to the flame can have adverse effects on its properties, e.g. increased background levels from carbon particles and band spectra.

The use of electrothermal atomization should circumvent the problem of low nebulization efficiency; however, the time required to run through an atomizer dry-ash-atomize-cool cycle results in only infrequent samples being analysed out of the flowing chromatographic stream. To minimize the possibility of missing a species, very low flow-rates are normally used and even so, not all the eluent is monitored. Hence recourse to indirect interfaces such as autosampler systems is often required and "real time" chromatographic interpretation is not possible. Thus direct coupling to a flame offers real time chromatographic interpretation but with low sensitivity detection whilst using electrothermal atomization high sensitivity detection is possible, but at the expense of real time analysis. The advent of microbore HPLC may provide some solution to problems with eletrothermal atomizers. Low flow-rates, microlitres per minute, encountered in microbore HPLC mean that the volume containing a species is very

small and providing the peak resolution is good, injection into the furnace of the whole chromatographic peak is feasible. Another possible, though expensive, way of making coupled HPLC-ETA-AAS a real time method would be to use a dual furnace system.

The same problems beset coupled LC-AFS as afflict any AFS method, namely: unavailability of commercial instruments,and suitably stable and intense line sources. However, the advent of a new atomic fluorescence instrument using an ICP as atom cell will perhaps signal a renewed interest and enable the advantages of multi-element low level detection afforded by AFS to be utilized.

The plasma emission techniques offer the possibility of multi-element detection and long linear ranges. With reverse phase eluents, both DCP- and ICP-OES, like FAAS, suffer from low nebulization efficiencies and to increase detectability, then this efficiency must be increased. The use of normal phase eluents affords high nebulization efficiencies and as a result a higher background emission level, and hence an increase in detection limits. This may be offset by the increased analyte flow into the plasma. The ability of plasmas to monitor not only metal emission lines, but also carbon lines, could, so long as non-carbon containing eluents are used, offer a universal LC detector. Although emphasis has been placed on the advantages of specific or at least selective detection, the uses of a universal detector should not be underestimated as the wide usage of FID in GC shows. By using the multi-element facility, DCP- or ICP-OES could very well prove to be the future universal detectors of LC.

4. INITIAL DEVELOPMENT OF ATOM CELLS FOR TRACE METAL SPECIATION BY GAS CHROMATOGRAPHY - ATOMIC ABSORPTION SPECTROSCOPY

4.1 CHOICE OF SPECIATION SYSTEM

4.1.1 Why Flame Atomic Absorption Spectroscopy?

The main advantages of using atomic spectroscopy in conjunction with gas chromatography may be summarised as below:

(i) The ability to perform selectively speciation of various individual metals and many non-metals;

(ii) The ability to withstand less than optimal GC conditions, i.e. only the species containing the element of interest require resolution from each other and need not be resolved from other components of the matrix;

(iii) With the exception of electron capture, most conventional detectors in GC are much less sensitive to metals than atomic spectroscopic detectors. The latter often enjoy detection limits in the picogram per second range.

The various atomic spectroscopic detectors have inherent in them various advantages and disadvantages; however, all have the attributes listed above. FAAS has the advantage of simplicity of atom cell design and operation. The instrumentation is relatively inexpensive and readily available in most laboratories concerned with the monitoring of metals. Flame atomic absorption spectroscopy is also noted for excellent selectivity. Any absorption technique suffers from having

short linear ranges, normally 1 - 2 orders of magnitude, and also, in the majority of published reports flame systems appear to produce relatively high detection limits. Electrothermal atomization AAS utilizes more expensive instrumentation, the atom cell is designed to accept small, 10 µl-100 µl, discrete condensed phase samples, and the heating of such devices is typically not continuous. Thus modification is required before it can accept a continuous flowing sample stream. The main benefit of this detection system is in the excellent limits of detection obtainable. Atomic fluorescence spectroscopic detectors, although not readily available, do offer improvements in detection and extended working ranges, typically four orders of magnitude, compared to AAS.

All the plasma emission techniques afford extensive linear working ranges, but fall short on detection limits particularly when compared to electrothermal atomization AAS. The plasma instrumentation is expensive both in capital outlay and running cost. The excitation cells, being made up of flowing gas streams, are well suited for interfacing with GC; however, the instrumentation is not readily available. Additionally, spectral background problems may necessitate specialist background correction modification to instrumentation.

From the above considerations, it was decided to use FAAS as the detector for GC with the aim of developing a simple, robust, sensitive hybrid GC-FAAS system.

4.1.2 Model Speciation System

The determination of tetraalkyllead compounds in petrol, besides being important from an environmental and toxicological viewpoint, offers a suitable model for trace metal speciation studies, since very little sample pretreatment is required, and the number of components of interest is small.

4.2 EXPERIMENTAL

4.2.1 Apparatus

Atomic Absorption Spectrometers:

SP 192 (Pye Unicam Ltd., Cambridge) equipped with deuterium arc background corrector and SP 198 rapid response interface.

SP 9 (Pye Unicam Ltd., Cambridge) equipped with hollow cathode lamp background correction.

Gas Chromatographs:

Series 104.

GCV equipped with dual flame ionization and electron capture

Series 303

All chromatographs supplied by Pye Unicam Ltd., and were equipped with temperature programme facilities.

Computing Integrators:

DP 88 (Pye Unicam Ltd., Cambridge)

3390 A Reporting Integrator (Hewlett Packard, Pennsylvania)

Ceramic Tubes:

Recrystallised Alumina (Thermal Syndicate Ltd., Wallsend)

4.2.2 Reagents

Stock solutions of tetramethyllead (TML) and tetraethyllead (TEL), containing 500 $mg.l^{-1}$ of lead, were supplied by Associated Octel Ltd., as was the CR50 mixture. This mixture contained TML, ethyltrimethyllead (ETML), diethyldimethyllead (DEDML), methyltriethyllead (MTEL) and TEL in the ratio 1:4:6:4:1 with a total lead concentration of 500 $mg.l^{-1}$. All dilutions were made using 2,2,4-trimethylpentane (Analar).

4.2.3 Initial Chromatographic Conditions

Glass Column:	1.5 m. x 4 mm. i.d.
Solid Support:	Chromosorb 750, 80/100 mesh
Stationary Phase:	Carbowax 20M, 5% loading
Column Temperature:	160°C
Carrier Gas:	Nitrogen, 40 $ml.min^{-1}$

4.2.4 Typical Spectrometer Conditions

	SP 192	SP 9
Air flow-rate /$l.min^{-1}$	4.5	5.0
Acetylene flow-rate /$l.min^{-1}$	1.2	1.3
Propane flow-rate /$l.min^{-1}$	0.3	-
Burner height[(a)] / mm	5.0	-
Lamp current / mA	3.0	4.2
Wavelength / nm	283.3	283.3
Mode	Abs.	Abs.
Bandpass / nm	0.8	1.0
Background Correction	ON	LOW

(a) The burner height is the distance between the centre of the optical path and the burner head, i.e. the viewing height.

4.3 PRELIMINARY CONSIDERATIONS

In conventional FAAS there are two main limitations on the achievement of low level detection. Firstly, low nebulization efficiency, whereby only about 15% of the analyte reaches the flame. Secondly, since a flame is a dynamic entity, the residence time of the analyte in the observation zone is short. In coupled GC-FAAS the first limitation is overcome easily since nebulization is not required as the analyte is already in the vapour phase. Although in GC-FAAS a continuous gaseous stream is introduced into the flame, thus eliminating the nebulization inefficiency, the analyte itself is transient in nature, thus further exacerbating problems concerning residence time. The latter aspect therefore becomes a vital consideration affecting both sensitivity and precision because of the response time of the electronics. The use of peak height or area measuring circuitry, which is less limited by conventional time constant considerations, is advantageous in monitoring transient signals.

Probably the simplest way to link a gas chromatograph with an atomic absorption spectrometer is to pass the effluent directly into the nebulization chamber. This was the coupling first demonstrated by Kolb *et al*. (161) using a short piece of heated tubing. Coker (167) used a slightly different method of interfacing whereby the chromatographic effluent was passed directly to the burner head by a heated metal transfer line connected to a gas union threaded into the side of the burner. A short manifold positioned inside the burner head was used to distribute the effluent evenly along an air/acetylene flame.

4.4 ATOM CELL I

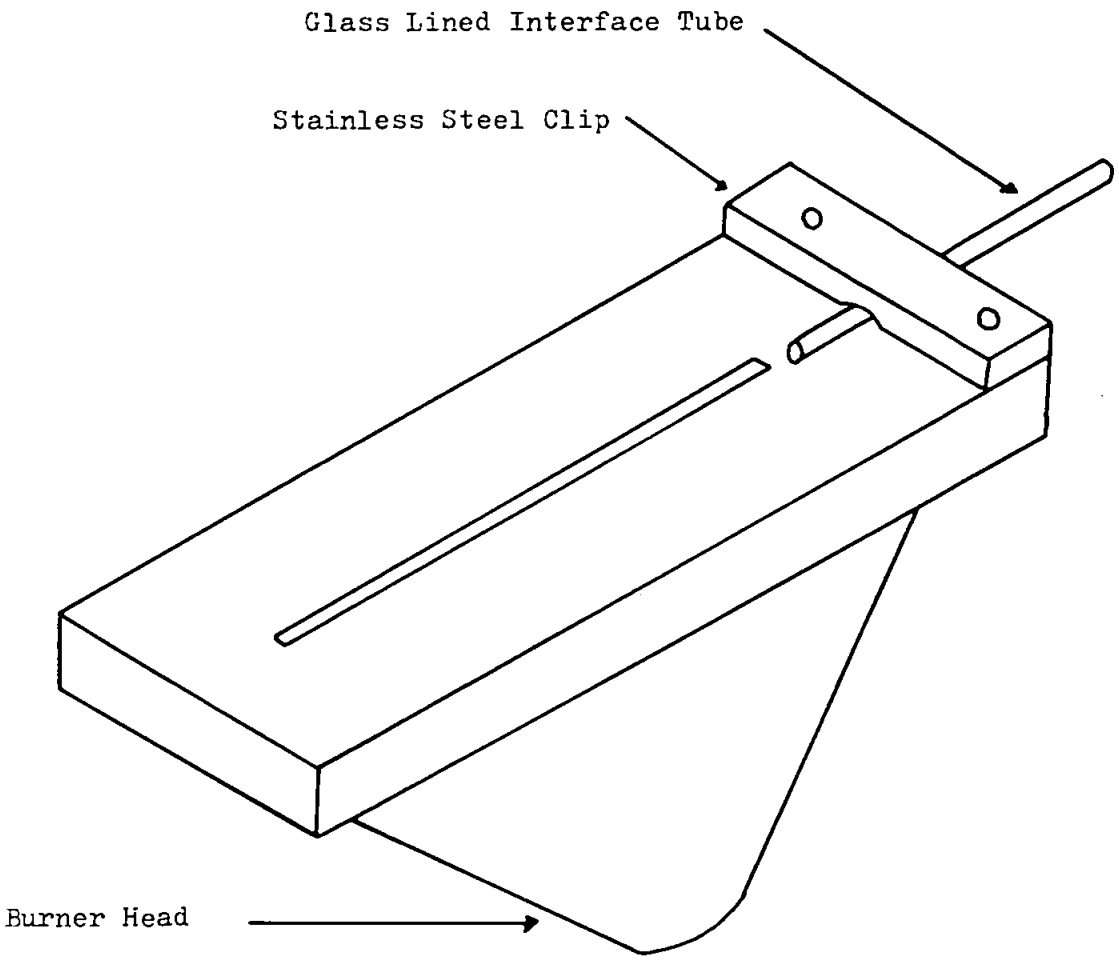
Preliminary work in which the effluent from the chromatograph was delivered directly to the mixing chamber of a conventional air/acetylene flame for AAS confirmed that although such an approach was feasible it involved unnecessary dilution of the effleunt. The interface used by Coker (167) was thought to be needlessly complicated, although it did avoid dilution mixing in the nebulization chamber.

Detectability was immediately improved when the effluent was passed directly to the flame. In atom cell I, fig. 1, the effluent from the chromatograph was passed down the heated glass lined tubing directly to the burner head, and impinged laterally on the analytical flame. The interface tubing was heated by a method similar to that of Quimby et al, (97), the power being supplied by a variac transformer and the temperature monitored by a standard thermocouple arrangement. The length of this interface tubing was varied between 18 and 55 cm. with no variation in response for either TML or TEL. If the interface was not heated, so as to be at least isothermal with the chromatographic column, the signal-to-noise ratio decreased as interface length increased, which was probably due to the oven heating circuit switching on and off more often.

As the solvent front impinged upon the air/acetylene flame it produced a luminous flare. Visual monitoring of this flare indicated that no more than 3 mm. of an available 100 mm. path length was being utilized. This is due to the flame gases sweeping the chromatographic effluent away from the burner and through the observation zone.

Figure 1

Atom Cell I



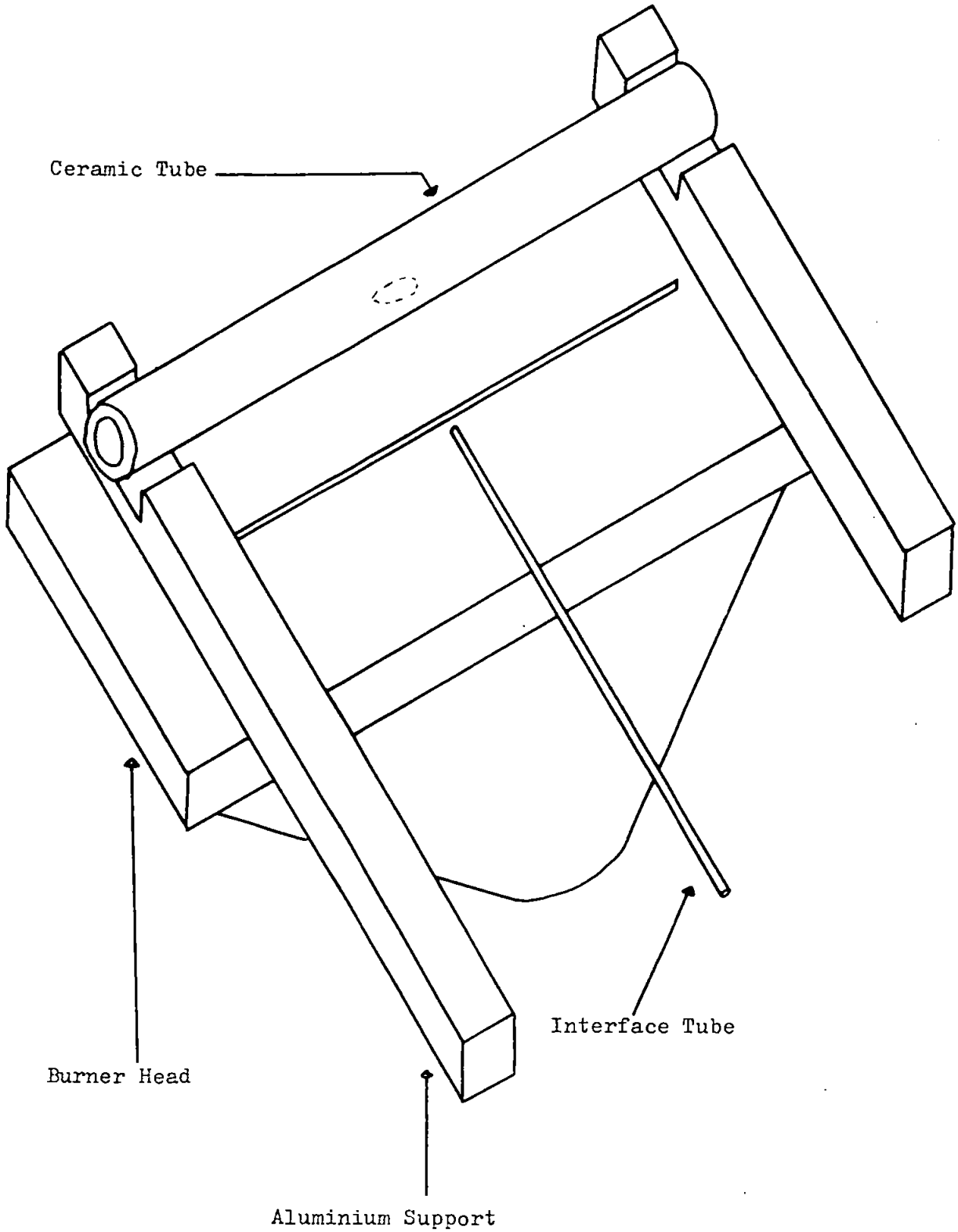
Clearly a slower burning flame would be expected to allow more of the available pathlength to be utilized. The air/propane flame has a burning velocity of 0.45 $m.s^{-1}$, compared with 1.6 $m.s^{-1}$ for the air/-acetylene flame (150). The use of an air/propane flame gave an immediate 3-fold increase in the response to lead. The low background argon (4 $l.min^{-1}$)/hydrogen (1.5 $l.min^{-1}$) diffusion flame was also studied, however, the lead response using this flame was less than that achieved with the air/acetylene flame. This could be expected since it has a burning velocity of 3.1 $m.s^{-1}$ which is greater than that of the air/-acetylene flame.

4.5 ATOM CELL II

The increased lead response gained by using the air/propane flame arose from the increased atomic residence time in the observation zone. It was thought that the response might be further improved by using a tube to hold the atoms in the observation zone longer. The use of such tubes has long been recognised to increase residence times (150, 154), and more recently, Watling (267) used a slotted tube in an atomic-absorption flame to increase not only sensitivity but also precision. The increase in sensitivity obviously arises from the increased residence time and given the likely time constant in the measuring circuit this also led to an improved precision. Delves (268) used a tube suspended above the flame in conjunction with a micro-sampling system to give increased sensitivity by increasing atom residence times in the light path. Therefore in an effort to increase atom residence times, atom cell II, fig. 2, was designed. This cell had a ceramic tube supported over the analytical flame on aluminium rods. There was a hole centrally placed in the bottom of the tube. The effluent from the

Figure 2

Atom Cell II



chromatograph passed via the heated glass lined interface so that it impinged on the analytical flame at right angles directly below the hole.

The ceramic tubes were constructed from recrystallised alumina and their dimensions are given in Table 10. The effect of ceramic tube internal diameter was investigated and from the results obtained, Table 11, it can be seen that the 6.25 mm. i.d. tube gave a two-fold increase in response to lead over the 12.5 mm. i.d. tube, and was therefore used in further work. The fact that the smallest diameter ceramic tube gave the best response may be attributed to increased viscous drag from the tube walls, and that the tube has less internal space unilluminated. These preliminary experiments showed that a 5-fold increase in response to lead over atom cell I had been achieved without optimisation of the system.

Table 10. Ceramic Tube Specifications

Length/mm.	Outer diameter/mm.	Internal diameter/mm.	Hole diameter/mm.
110	16.0	12.5	10.0
110	14.5	10.0	8.0
110	12.5	8.0	6.0
110	10.0	6.25	4.0

Table 11. Effect of Ceramic Tube Internal Diameter on Lead Response

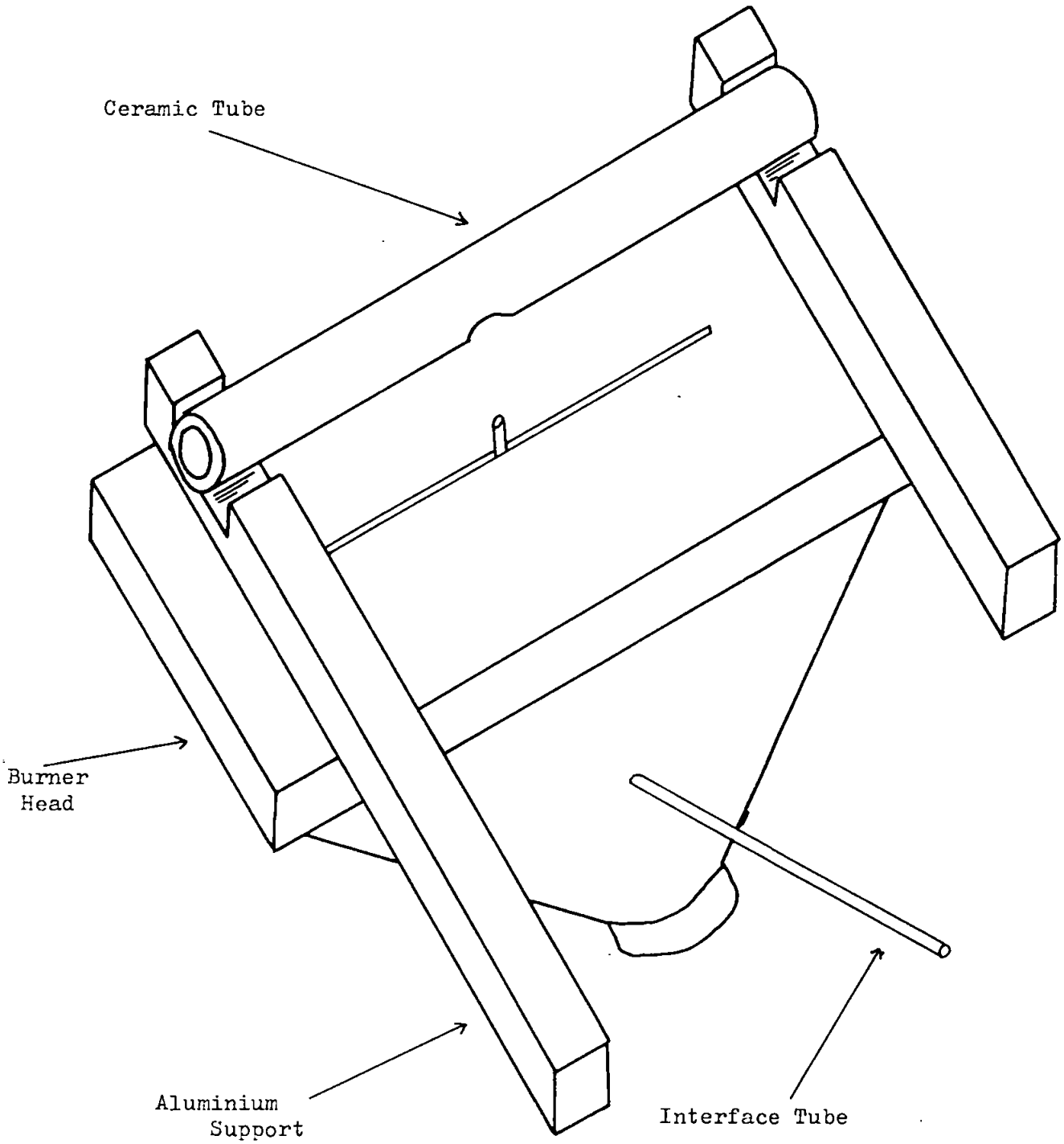
Ceramic tube i.d./mm.	Relative Lead Response	
	TML	TEL
12.5	1.0	1.0
10.0	1.1	1.1
8.0	1.6	1.7
6.25	1.9	2.1

4.6 ATOM CELL III

Visual monitoring of the luminous flare produced as the solvent impinged on the flame showed that some of the chromatographic eluent was passing around the outside of the ceramic tube. Thus, in order to ensure that all the effluent passed into the light path of the spectrometer, a further atom cell was developed. Atom cell III, fig. 3, retained the ceramic tube above the flame to help increase residence times, and incorporated the refinement of the interface tube passing through the burner and terminating just above the burner slit directly below the hole in the ceramic tube. The advantage over atom cell II was that the chromatographic effluent possessed some directional impetus towards the hole in the ceramic tube. The best distance above the burner slot at which to terminate the interface was found to be 1 mm. so as to ensure direct delivery into the hot flame rather than the unburnt gases. Preliminary results with this atom cell indicated that a further slight increase in response to lead had been achieved.

Figure 3

Atom Cell III



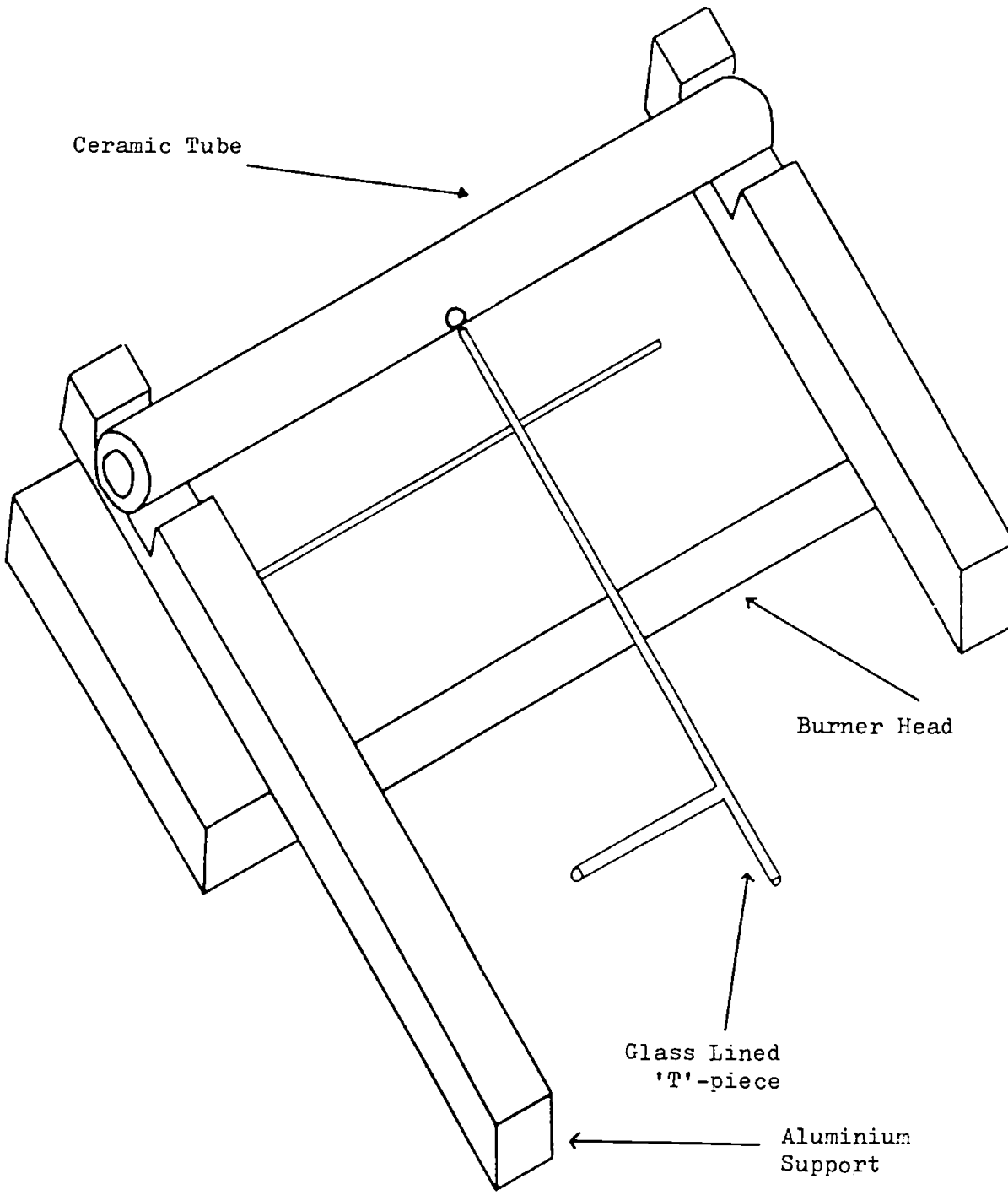
4.7 ATOM CELL IV

In atom cells II and III the air/acetylene flame performed two functions: firstly, atomization of the alkyllead species, and secondly, heating of the ceramic tube to prevent condensation of the atomic species. However, in these cells the exhaust gases of the flame also passed down the ceramic tube. In an attempt to prevent this and hence increase the residence time of the atoms in the tube, atom cell IV, fig. 4, was developed, in which the atomization and tube heating functions were separated.

In atom cell IV the ceramic tube arrangement over the analytical flame was the same as for atom cell II, except that the hole was in the side of the tube, i.e. at right angles to the burner head. The gas chromatographic effluent passed along the interface tube to a glass lined 'T'-piece into which an auxilliary flow of hydrogen was introduced. A miniature hydrogen diffusion flame was burnt on the end of the 'T'-piece. This flame was aligned with the centre of the hole in the ceramic tube. Thus, the air/acetylene flame heated the ceramic tube to prevent condensation of the atomic species which were produced in the hydrogen diffusion flame.

Figure 4

Atom Cell IV



4.8 ATOM CELL V

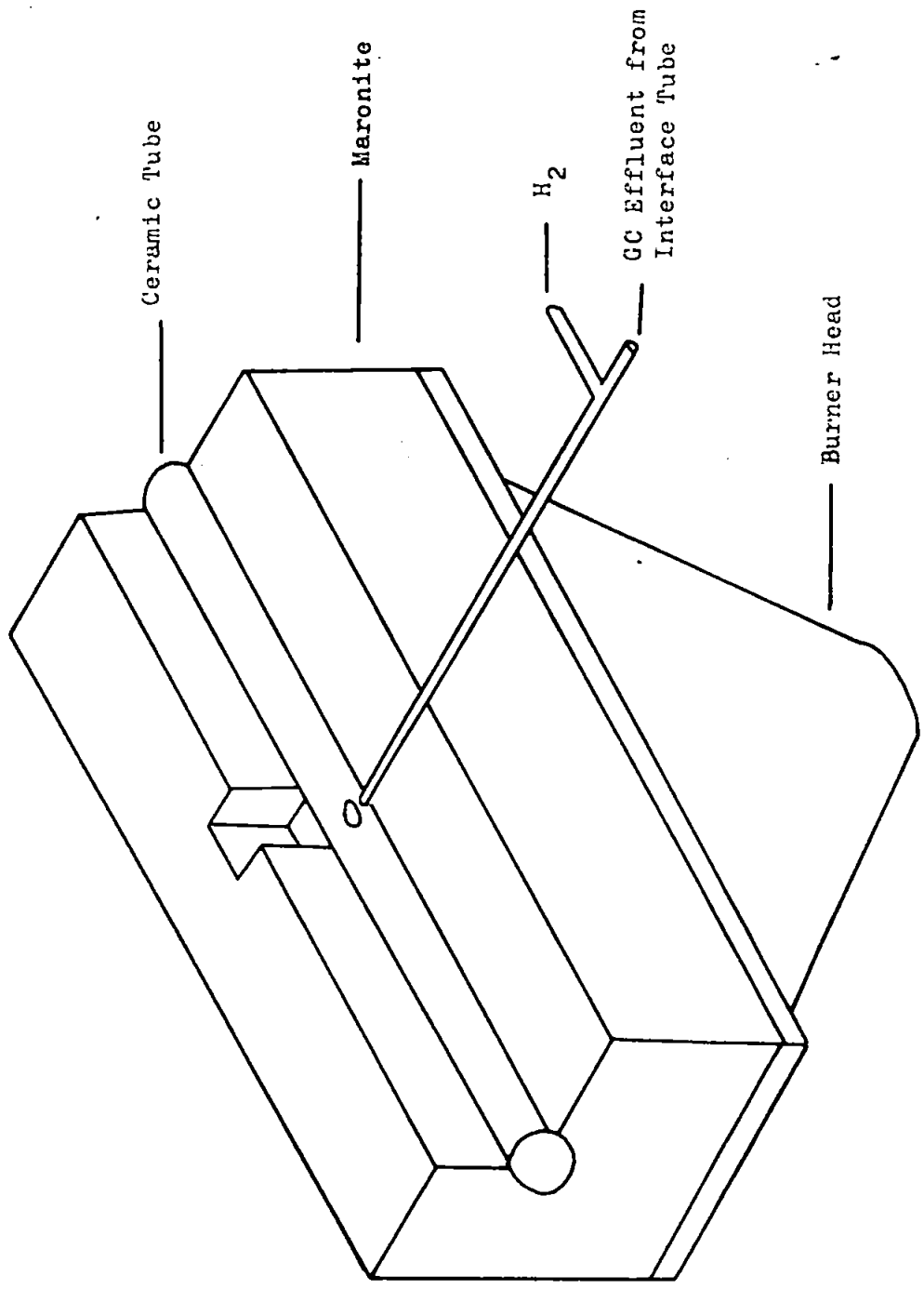
To enable the merits of the simple flame atom cells developed to be fully evaluated, an electrothermally heated varient of the last atom cell was prepared. In atom cell V, fig. 5, the ceramic tube was electrothermally heated by two Nichrome wire ($2.8\Omega\ m^{-1}$) windings connected in series with a transformer which had a variac voltage supply (0-60 V). The tube plus windings were wrapped in glass wool and placed inside a maronite block. This block was then attached to a standard burner head by spring clips and aligned in the optical path of the spectrometer.

Preliminary work showed this atom cell to be a viable atom cell and the response to lead was found to be equivalent to that found with atom cell IV.

The rapid development from the very simple atom cell I to atom cell V enabled only cursory comparison of analytical performance, and no evaluation of their relative merits. To enable valid comparisons to be made, the operating parameters of the various atom cells must be optimized. This optimization will be discussed in the next chapter.

Figure 5

Atom Cell V



5. OPTIMISATION STUDIES

5.1 OPTIMISATION STRATEGY

True comparison of the analytical performance of different atom cells can only be made when those atom cells have been rigorously optimised. Unfortunately, this is not always done, probably because a factorial design of optimisation experiment may be both tedious and time-consuming. If attempts are made to give certain factors priority, the factorial optimisation may be more rapid, but there is an attendant risk of not obtaining the true optimum. Thus, it was decided to use a simplex procedure (269-275) for the atom cell optimisation.

5.1.1 Simplex Optimisation

A simplex is a geometrical figure, defined by a number of points in factor space. Thus, an n dimensional simplex will be defined by n + 1 points in factor space. For the simplest multifactor problem, namely an optimisation of two parameters, the simplex is a triangle. The response at the vertices of the triangle are evaluated and the worst one rejected. A new simplex triangle, is generated by reflection away from the worst vertex through the centroid point of the remaining vertices. The response at the new vertex is then evaluated. The simplex procedure continues by successive rejection of the worst vertex followed by reflection away from the areas of low response. In the original simplex method (275), the step size between vertices was fixed. If this step size is too small compared to the factor spaced, then the optimum will be approached slowly; if it is too large, then the optimum will be imprecisely located. This is more noticeable when the simplex is a

geometrical figure which does not close pack, e.g. a tetrahedron. Since the step size is fixed, it is possible for the optimum to lie in unexplorable factor space between two simplex tetrahedra. The close identification of the optimum requires another simplex to be initiated with a smaller step size around the provisional optimum. Thus, this method normally requires at least two simplexes to be initiated and the modified simplex method, MSM, (269, 271) in which the step size is variable throughout, provides a more efficient and elegant solution. This variation in step size also avoids the achievement of a false or provisional optimum since it will allow close packing.

The modified simplex method can be simply visualised by considering a two-variable optimisation for which the original simplex, Fig. 6, is the triangle BNW. B represents the vertex giving the best response, N is the vertex giving the next best response and vertex W is the vertex of worst response. Instead of the single reflection of the basic simplex method, the MSM allows movement of the simplex in one of four alternate ways, Fig. 6. Each vertex of the triangle may be defined by a positional vector, $\bar{B}$, $\bar{N}$ and $\bar{W}$ respectively, where

$$\bar{B} = (X_b, Y_b)$$

$$\bar{W} = (X_w, Y_w)$$

$$\bar{N} = (X_n, Y_n)$$

Thus, the basic step may be defined as:

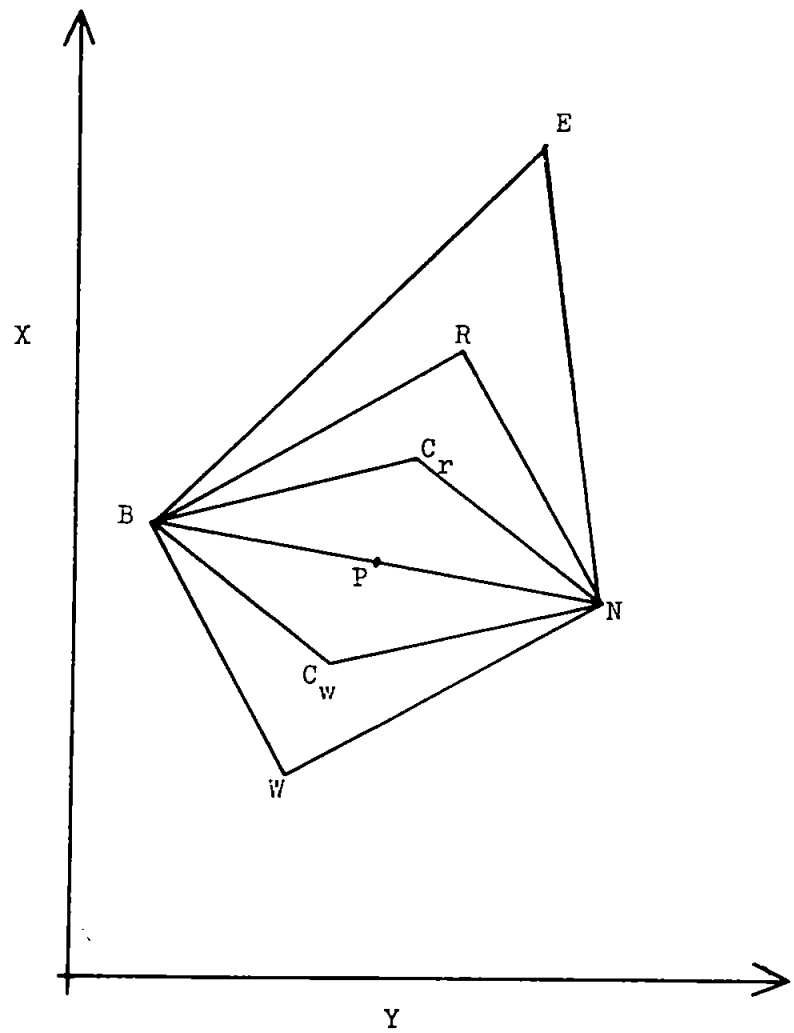
$$\bar{R} = \bar{P} + (\bar{P} - \bar{W}) \qquad \ldots 5(1)$$

where P = the centroid point of the line joining B and N

and R = new simplex vertex.

Figure 6

Possible Movements Allowed in the Modified Simplex Method



This step is equivalent to the basic reflection in the original simplex method. It would seem reasonable to assume that if the response at R gave a better response than B, the simplex was moving towards a favourable area of factor space. Thus, the MSM allows an expansion of the simplex defined by:

$$\bar{E} = \bar{P} + a(\bar{P} - \bar{W}) \qquad \ldots 5(2)$$

where a = expansion factor, normally a = 2

E = expansion vertex.

Similarly, if the response at R is less than at N, then it would appear that the simplex was moving towards an unfavourable area of factor space. Thus, movement away from R is indicated. The MSM allows two types of contraction, defined by:

$$\bar{C}_r = \bar{P} + b(\bar{P} - \bar{W}) \qquad \ldots 5(3)$$

where b = a contraction factor and $0 < b < 1$, typically b = 0.5

and

$$\bar{C}_w = \bar{P} - b(\bar{P} - \bar{W}) \qquad \ldots 5(4)$$

The choice of which of the above vertices with which to form the next simplex is governed by the following rules, after the analytical response has been evaluated for the vertices B, N, W and R.

Let the responses at the vertices be B^1, W^1, N^1 and R^1, where $B^1 > N^1 > W^1$. Thus, four possibilities for R^1 exist;

for $R^1 > B^1$ ... 5(5)

In this case, an expansion of the simplex is indicated, and the new vertex E, with response E^1, is generated.

Thus, if $E^1 > B^1$ then E is used to generate a new simplex, defined by the positional vectors $\bar{B}\ \bar{N}\ \bar{E}$. If $E^1 < B^1$ then the expansion is said to have failed, and R is used to generate the new simplex, defined by $\bar{B}\ \bar{N}\ \bar{R}$, and the algorithm restarted.

$$\text{for} \quad B^1 > R^1 > N^1 \qquad \ldots \quad 5(6)$$

then neither expansion nor contraction is indicated, and new simplex is defined by $\bar{B}\ \bar{N}\ \bar{R}$ and the algorithm restarted from these points.

$$\text{for} \quad N^1 > R^1 > W^1 \qquad \ldots \quad 5(7)$$

Then a contraction of the simplex is indicated away from both $\bar{W}$ and $\bar{R}$, thus C_r is generated, and used in the new simplex, $\bar{B}\ \bar{N}\ \bar{C}_r$, and the algorithm restarted:

$$\text{for} \quad W^1 > R^1 \qquad \ldots \quad 5(8)$$

A contraction away from $\bar{R}$ and towards $\bar{W}$ is indicated, generating C_w with the new simplex being $\bar{B}\ \bar{N}\ \bar{C}_w$.

If any of the variables which make up the simplex vectors $\bar{R}$, $\bar{C}_w$, $\bar{C}_r$ and $\bar{E}$ lie outside the boundary condition for that variable, then the response at that point is assigned an artificially low value, and the algorithm continued.

A failed contraction is said to occur if $C_r{}^1 < R^1$ or if $C_w{}^1 < R^1$. In this event, Nelder and Mead (269) recommended a massive contraction to avoid oscillatory collapse of the simplex. This contraction, although effective, requires the generation of n new simplex vertices before the algorithm may continue, and also reduces the volume of factor space covered by the simplex by a factor of $(0.5)^n$. This latter fact may, in the presence of experimental error, cause premature contraction of the simplex. An alternative way of dealing with a failed contraction

(276) is to use the contraction vertex to generate the new simplex and to reject the worst vertex, W. This has the combined effect of preventing oscillatory collapse and also realignment of the simplex. It is really a reintroduction of Rule 2 of Spendly et al. (277), and has been used effectively by Morgan and Deeming (278) in a related field.

If a vertex is retained in n + 1 simplexes, then before evaluation of another simplex this vertex must be reevaluated. If the vertex is near the optimum it is probable that the reevaluation will yield a consistently high response, and hence be retained. If, however, the response was high due to an error in measurement, then it is improbable that the reevaluation will also give a high response, and thus the vertex will eventually be eliminated from the simplex.

A number of methods (269-272, 279) have been suggested as convergence criteria, i.e. when to halt the simplex procedure. The technique found to be most careful for our work was that of Dewer and student (279). The prime criterion being that of the variation in analytical response among the n + 1 simplex vertices is below a preset value, in this case $\pm$5%. After this is achieved, the response at the centroid of the entire simplex is evaluated, and the variance from this point used as the final convergence criterion, i.e. if below $\pm$5% the simplex procedure is halted. This method also found favour with Ryan et al. (273) in their comparison of simplex techniques for non-linear optimisation in analytical chemistry.

More recently, there have been further modifications to the variable step size simplex to improve its efficiency in reaching the optimum (272, 273). Ryan et al. (273) demonstrated that the super modified

simplex, SMS, (272) controlled weighted centroid method, CWC, and orthogonal jump weighted centroid method, OJWC (273), do indeed find the neighbourhood of the optimum more rapidly than MSM, but are less efficient when forced to identify the optimum point itself. The reason for this is probably that the CWC, SMS and OJWC make more use of the information found about the gradient of the response surface than does the MSM. Thus they should locate the general region of optimum response more rapidly; however, as the optimum is approached, the gradient direction becomes poorly defined, and of necessity at the optimum the gradient is zero, and thus attempts to use gradient information becomes fruitless and precise definition of the optimum is difficult.

The MSM allows for rapid attainment, close definition of the optimum and, because of its variable step size, prevents achievement of a false optimum. The choice of initial step size is critical in this optimization procedure. Yarbro and Deming (280) have shown it to be preferable to initiate the procedure with a large step size. This ensures the exploration of the maximum factor space prior to the simplex collapsing onto the optimum. These workers (280) described a matrix and the accompanying equations required to construct the initial simplex. Confirmation of the success of the optimisation procedure could obviously be found by initiating another optimisation from a different initial simplex. Winefordner and co-workers (281) offered another viable confirmation procedure, namely a series of univariate searches. For a univariate search (n - 1) of the n variable are held at their optimum values, and the remaining one varied across its allowed range of values as the analytical response is measured. This procedure was chosen because in addition to confirming the optimum, it also gave response curves for

each variable, so that an insight was gained as to the influence of each variable on the performance of the atom cell.

5.2 CRITERION OF MERIT FOR OPTIMISATION

5.2 Separation of Two Species

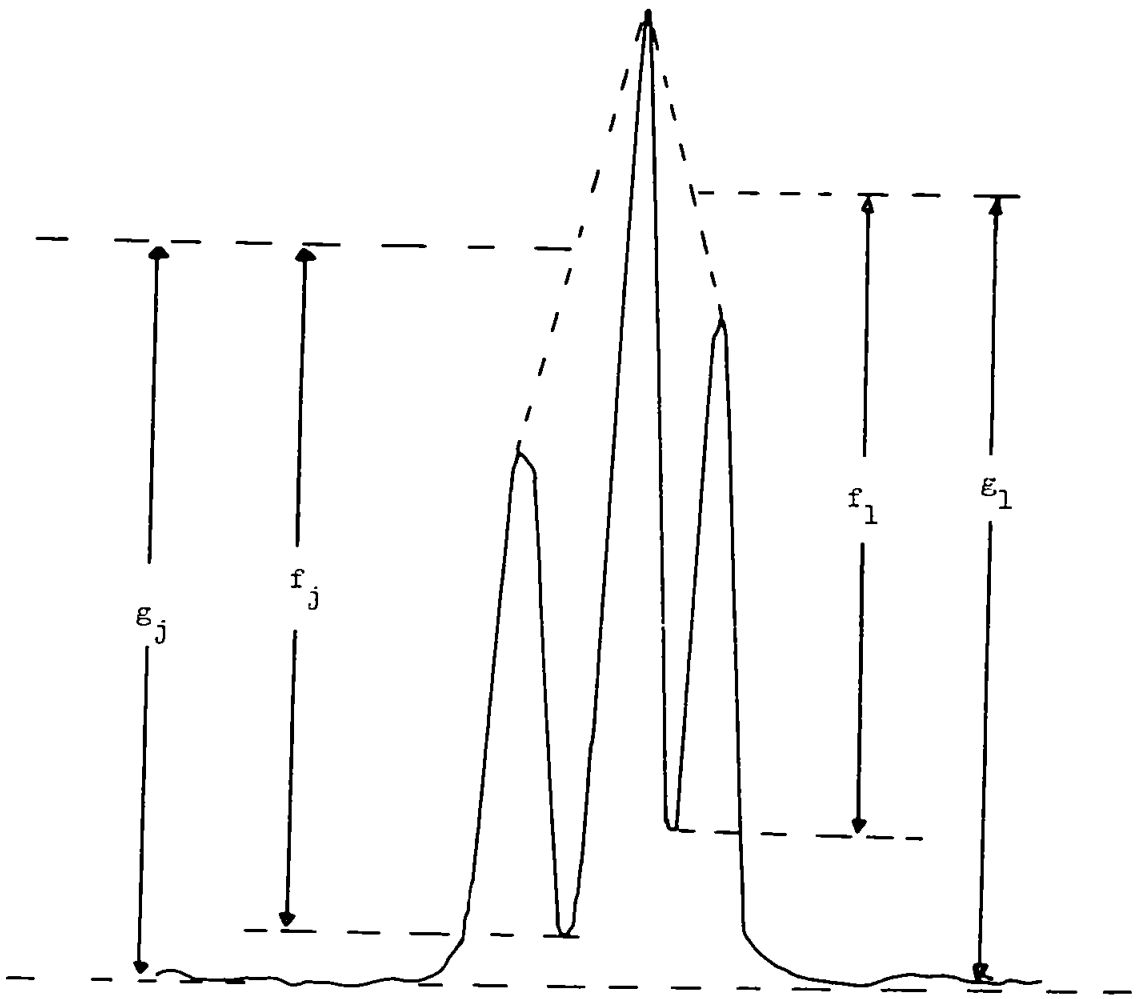
For the optimisation of the atom cells, the determination of TML and TEL was used. The criterion of merit chosen was peak height, subject to base-line resolution of the two species being obtained; no consideration of resolution or column efficiency was attempted. It was considered that by using peak height rather than peak area, a better indication of the system likely to yield the best limit of detection would be given.

5.2.2 Separation of n Species

For multi-component mixtures, e.g. the five mixed lead tetraalkyls, the criterion of merit used was the chromatographic response function (CRF) proposed by Morgan and Deming (278). This criterion, illustrated in figure 7, when minimised actually optimises for baseline resolution of all species. Thus, it is possible to visualise two chromatograms in which all species are fully resolved, but where analysis times are vastly different, figure 8. Thus, a further constraint was placed on the optimisation criterion, which was that the retention time should be as short as possible. This ensures that the system is optimised for resolution of the chromatographic peaks whilst giving the shortest analysis time.

Figure 7

The Chromatographic Response Function



$$P = f/g$$

$$CRF = \sum_{i=1}^{j} \ln (P_j)$$

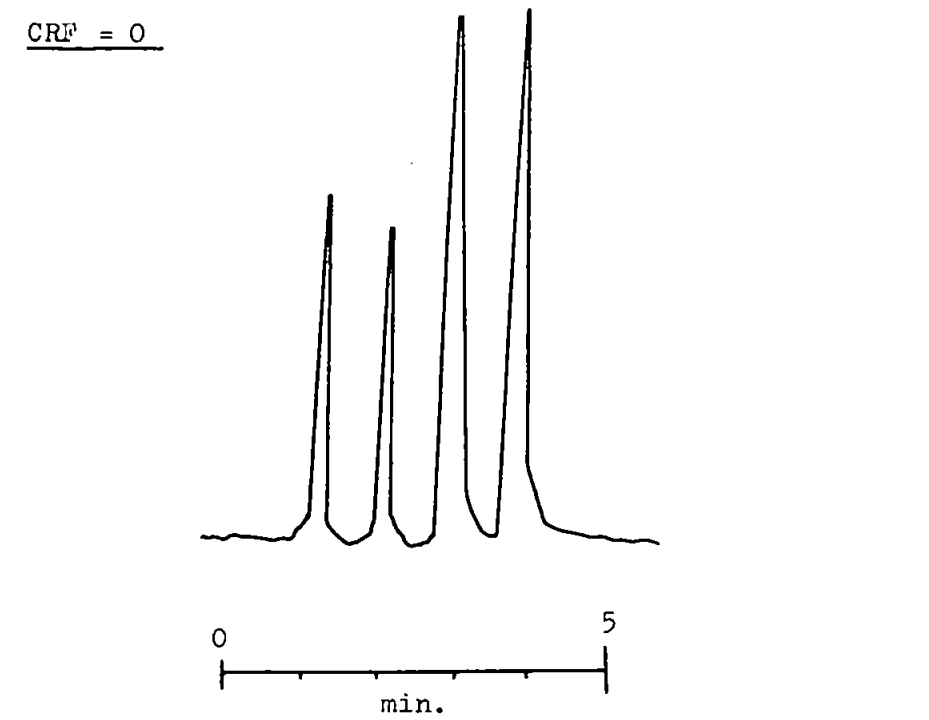
for complete separation;

$$P = 1$$

$$CRF = 0$$

Figure 8

Illustration of Two Different Chromatograms with Minimal Chromatographic Response Functions



5.3 RESULTS OF OPTIMISATION STUDIES

5.3.1 Atom Cell I

The continuously variable parameters investigated for this system were nitrogen carrier gas flow-rate, fuel gas flow-rate, air flow-rate, chromatographic column temperature and the distance of separation between the burner head and the centre of the optical path. The centroid of the optimum range identified by the simplex optimisation is given for each variable in Table 12, column 1. That the optimum had been achieved was then confirmed, using the univariate search procedure.

Figure 9 [(a) - (e)] demonstrate the success of the optimisation procedure. The shaded region on each graph identifies the optimum range predicted by the simplex procedure for each variable. Fig. 9(a) shows the carrier gas flow-rate to be a critical variable and confirmed the simplex predicted optimum. At first sight, it appeared strange that the optimum nitrogen flow-rate was so low, considering that the aim was to use as much of the available path length in the flame as possible. The low burning velocity of the air/propane flame confirmed the advantage of longer atom residence times, but also a certain lack of laminarity. Thus, high carrier gas flow-rates resulted in severe distortion of the flame profile, on occasion out of the light path, and hence yielded a low response to lead. Fig. 9(b) and (c) illustrate an interesting effect at high oxidant-to-fuel ratios. The univariate search for the oxidant flow-rate, fig. 9(b), shows that at high air flow-rates the peak-height response to lead for TEL decreased, probably owing to reduced flame temperature and hence reduced atomization efficiency. This effect was not noticed for TML. Although not observed using this

Table 12 Centroid Values obtained for the Simplex Variables in Atom Cells I - IV

Variable	Atom Cell			
	I	II	III	IV
Nitrogen flow rate/ml.min^{-1}	25	41	80	64
Propane flow rate/ l.min^{-1}	0.11	-	-	-
Acetylene flow rate/ l.min^{-1}	-	0.62	0.52	0.54
Air flow rate/l.min^{-1}	3.2	4.7	3.9	3.7
Hydrogen flow rate/ml.min^{-1}	-	-	-	40
Chromatographic Column Temperature/^{o}C	175	163	165	159
Viewing Height/mm.	4.1	-	-	-
Ceramic tube - air/acetylene burner separation/mm.	-	4.3	4.3	10.9
Ceramic tube - hydrogen diffusion burner separation/mm.	-	-	-	0.25

Figure 9(a)

Atom Cell I

Univariate Search for Nitrogen Flow-Rate

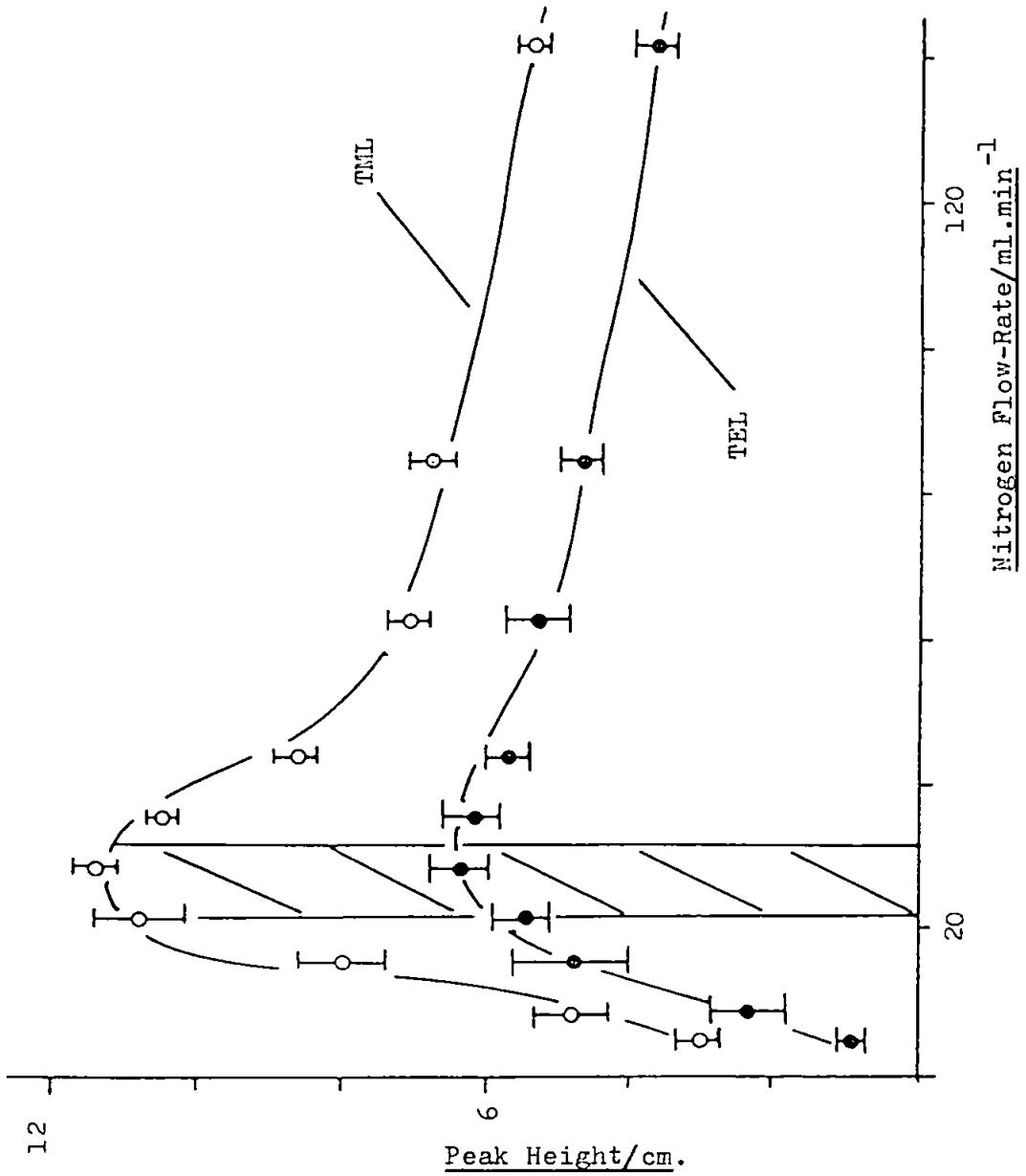


Figure 9(b)

Atom Cell I

Univariate Search for Air Flow-Rate

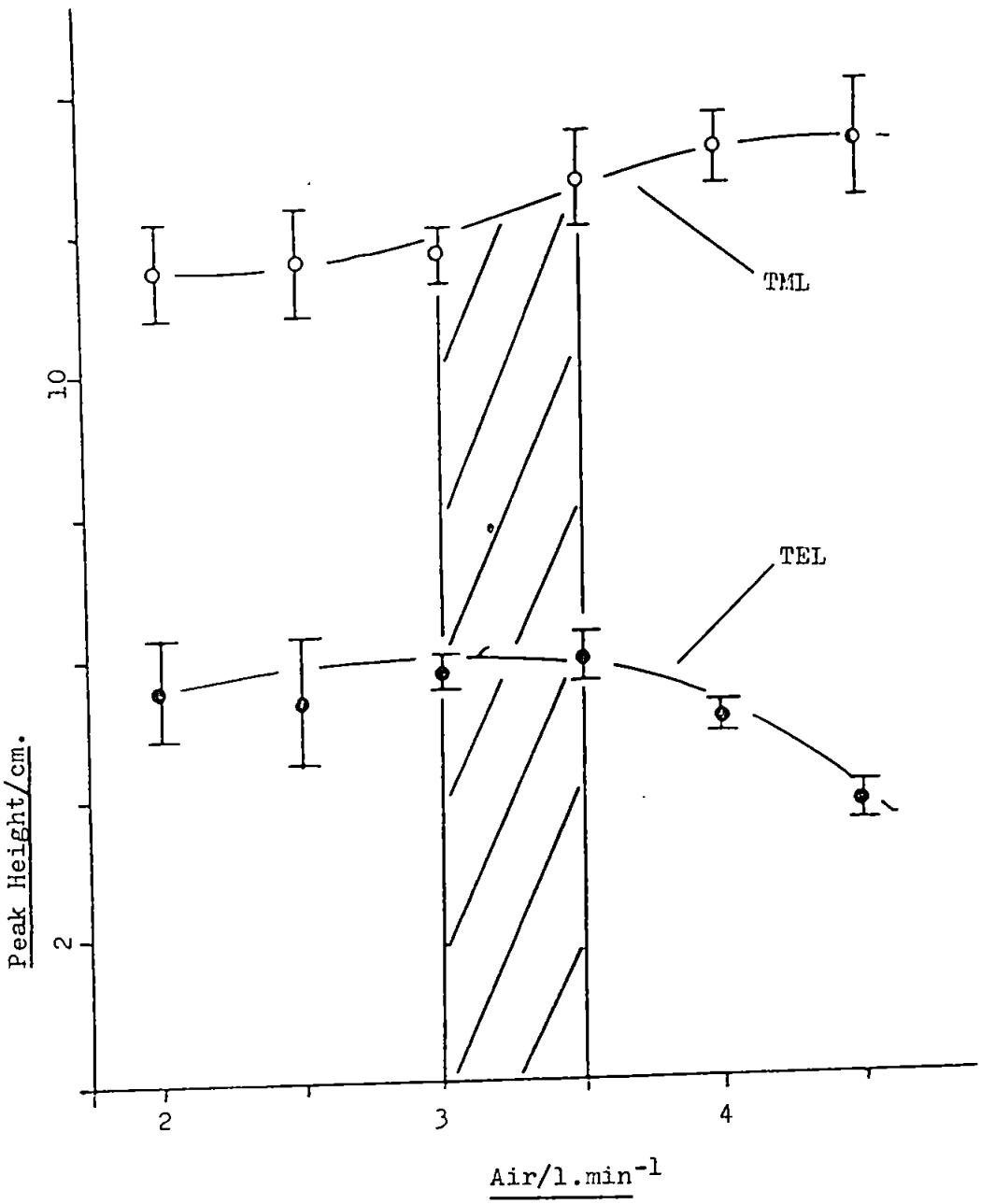


Figure 9(c)

Atom Cell I

Univariate Search for Propane Flow-Rate

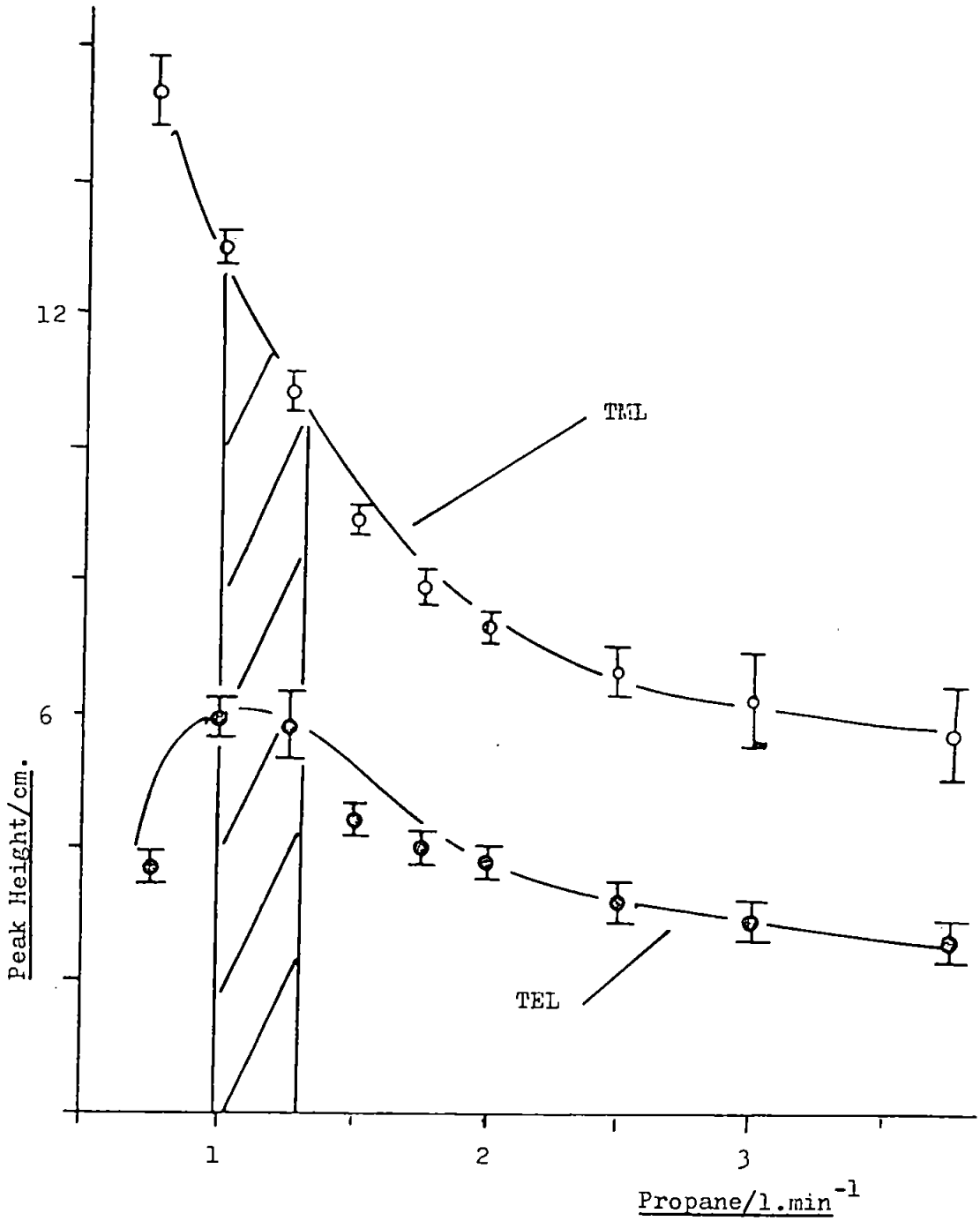


Figure 9(d)

Atom Cell I

Univariate Search for Chromatographic Temperature

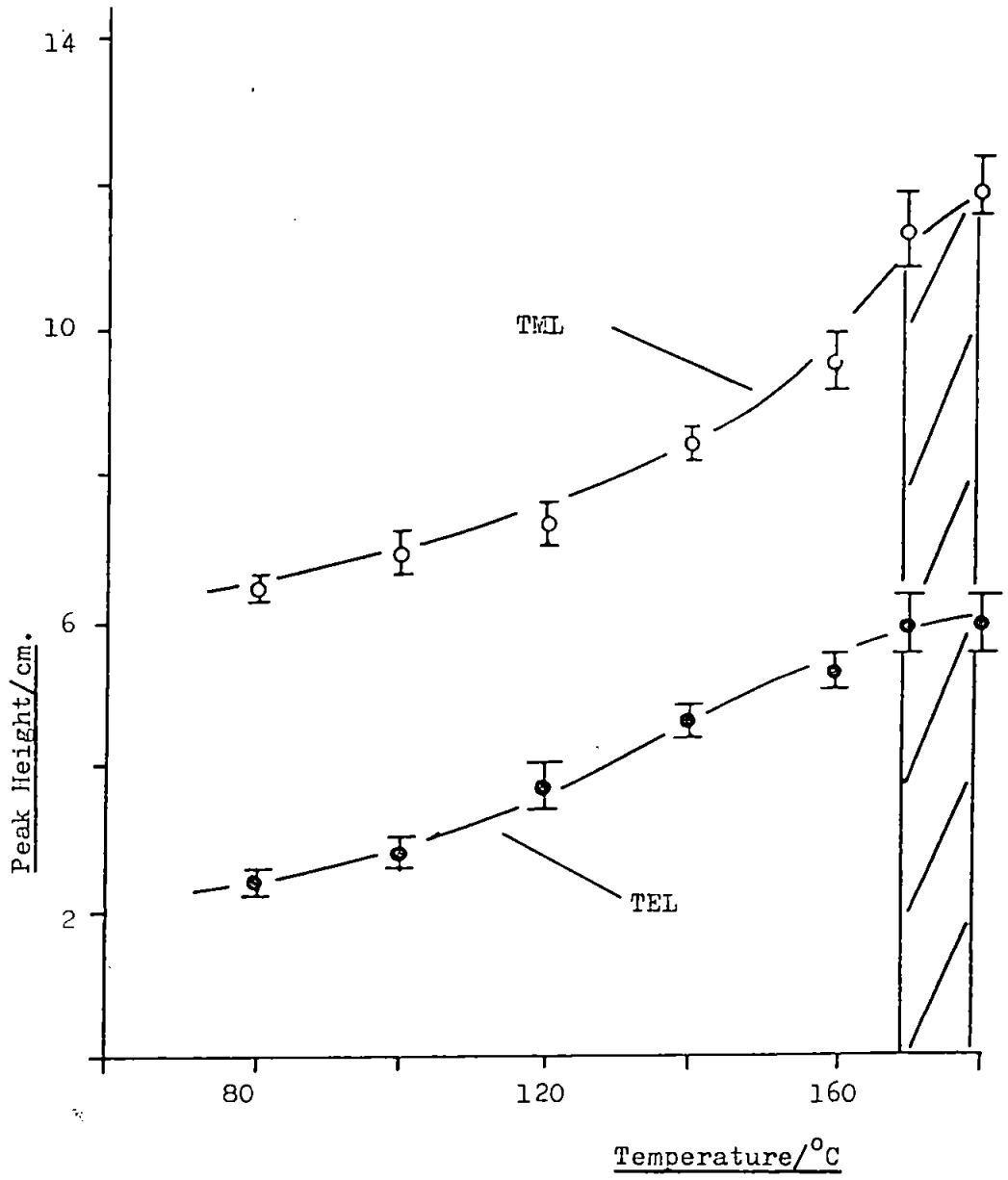
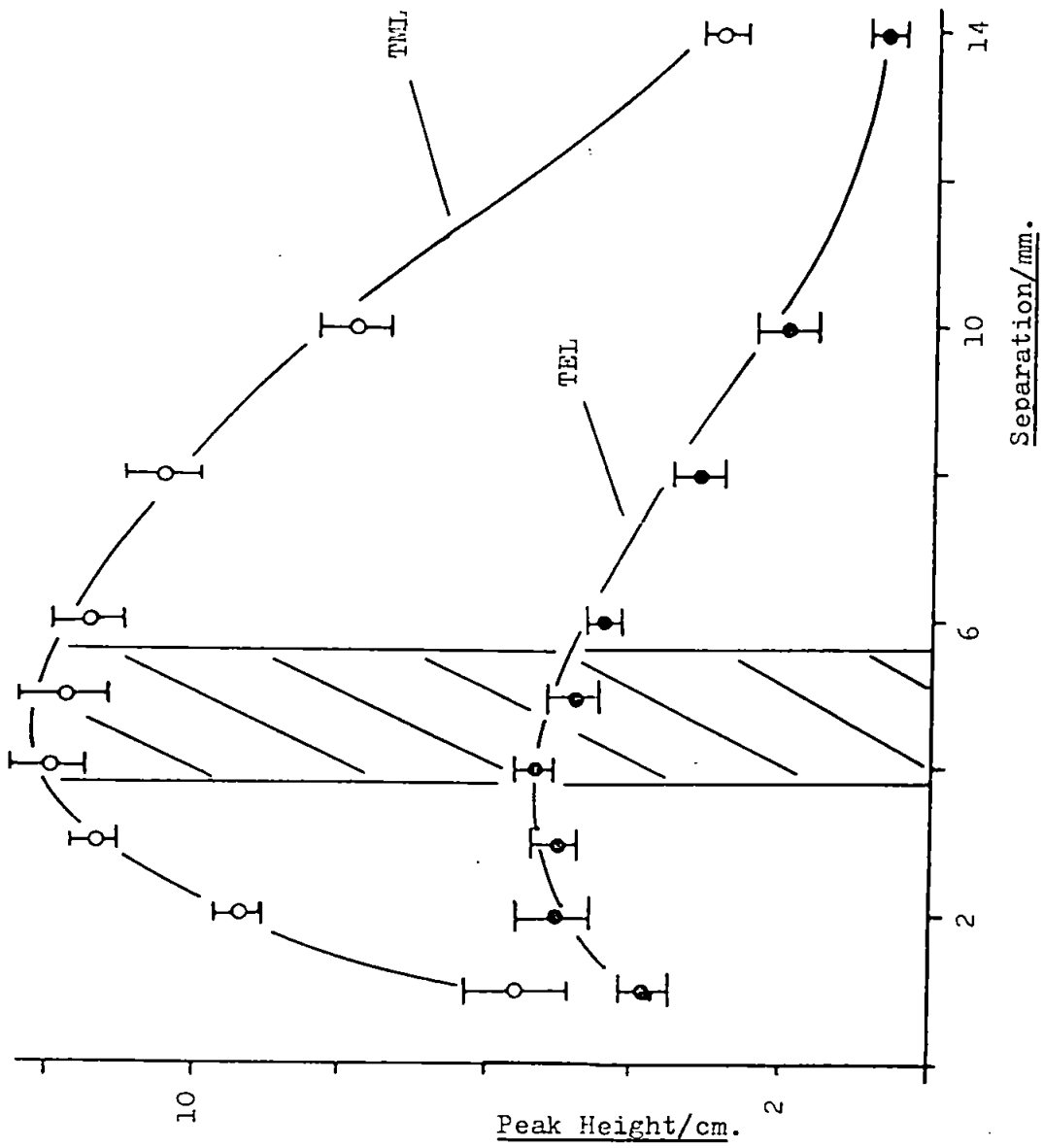


Figure 9(e)

Atom Cell I

Univariate Search for the Viewing Height



atomic absorption detector, the solvent peak overlaps the TML peak and thus may act as a secondary fuel aiding atomization. A similar effect was noted for the univariate search for the propane flow-rate, fig. 9(c), where at less than 100 ml min^{-1} of propane, the peak height for TEL decreased, whereas for TML it increased. This again would appear to be related to the effect of the solvent on the atomization process. The univariate search for the chromatographic column temperature, fig. 9(d), confirmed the predicted optimum range. This temperature range was the highest possible compatible with full base-line resolution of peaks, whilst also yielding the most rapid analysis times. This behaviour was also observed in the succeeding simplex optimisations. Fig. 9(e), showed the optimum distance of separation of the burner head and the centre of the optical path, i.e. the viewing height, to be just above the primary cones of the flame.

5.3.2 Atom Cell II

Only continuously variable parameters are amenable to simplex optimisation. Thus, choice of the best ceramic tube i.d. to use was made prior to simplex optimisation, see Chapter 4. The continuously variable parameters were nitrogen carrier gas flow-rate, oxidant (air) flow-rate, acetylene flow-rate, chromatographic column temperature and the separation between the burner head and the ceramic tube, placed in the centre of the optical path. The centroid values of the optimum range obtained for each variable from the simplex optimisation are given in Table 12, column 2.

The univariate searches, fig. 10 (a) - (e) illustrate the success of the optimisation procedure; the shaded regions on the graphs again

Figure 10(a)

Atom Cell II

Univariate Search for Nitrogen Flow-Rate

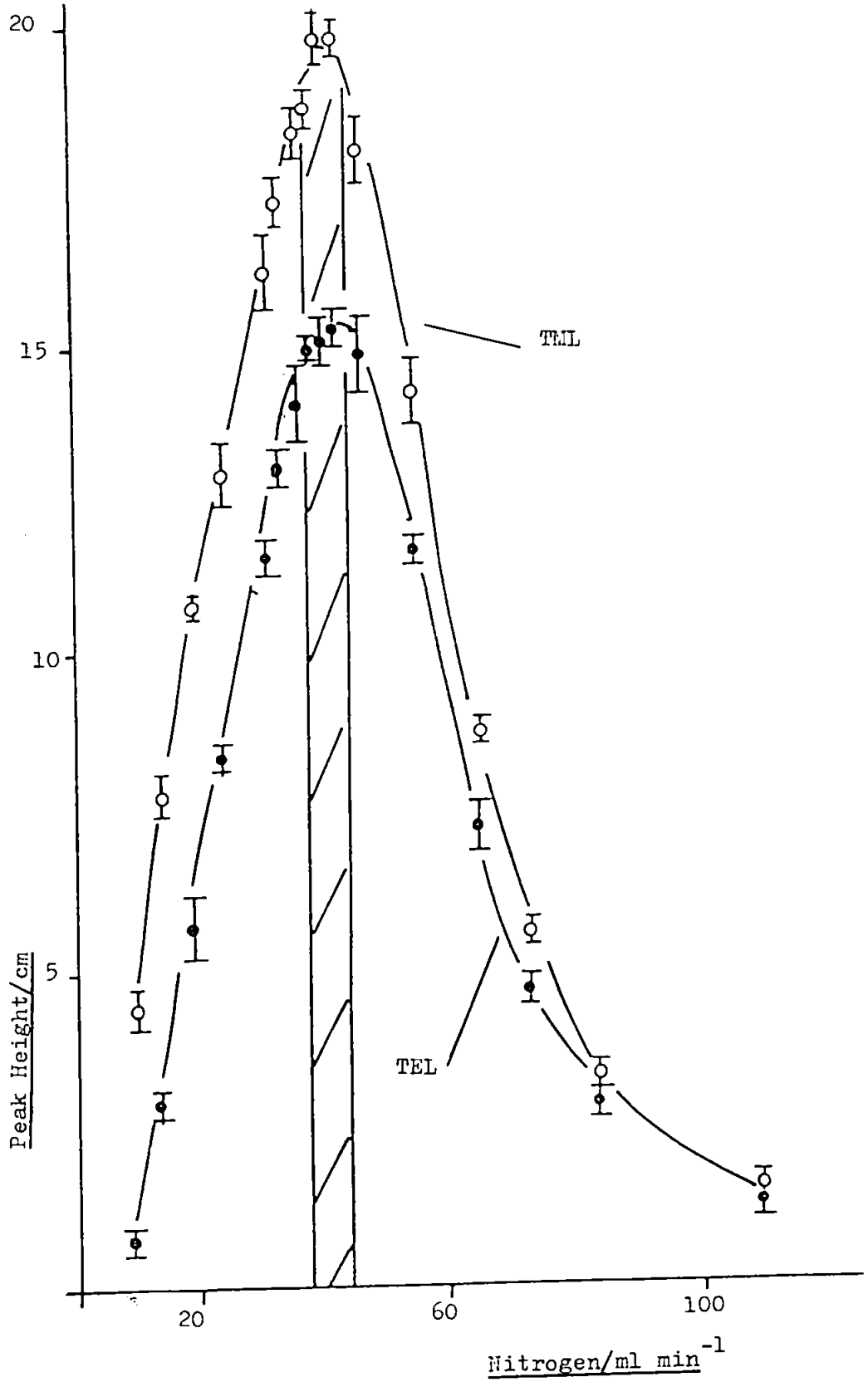


Figure 10(b)

Atom Cell II

Univariate Search for Air Flow-Rate

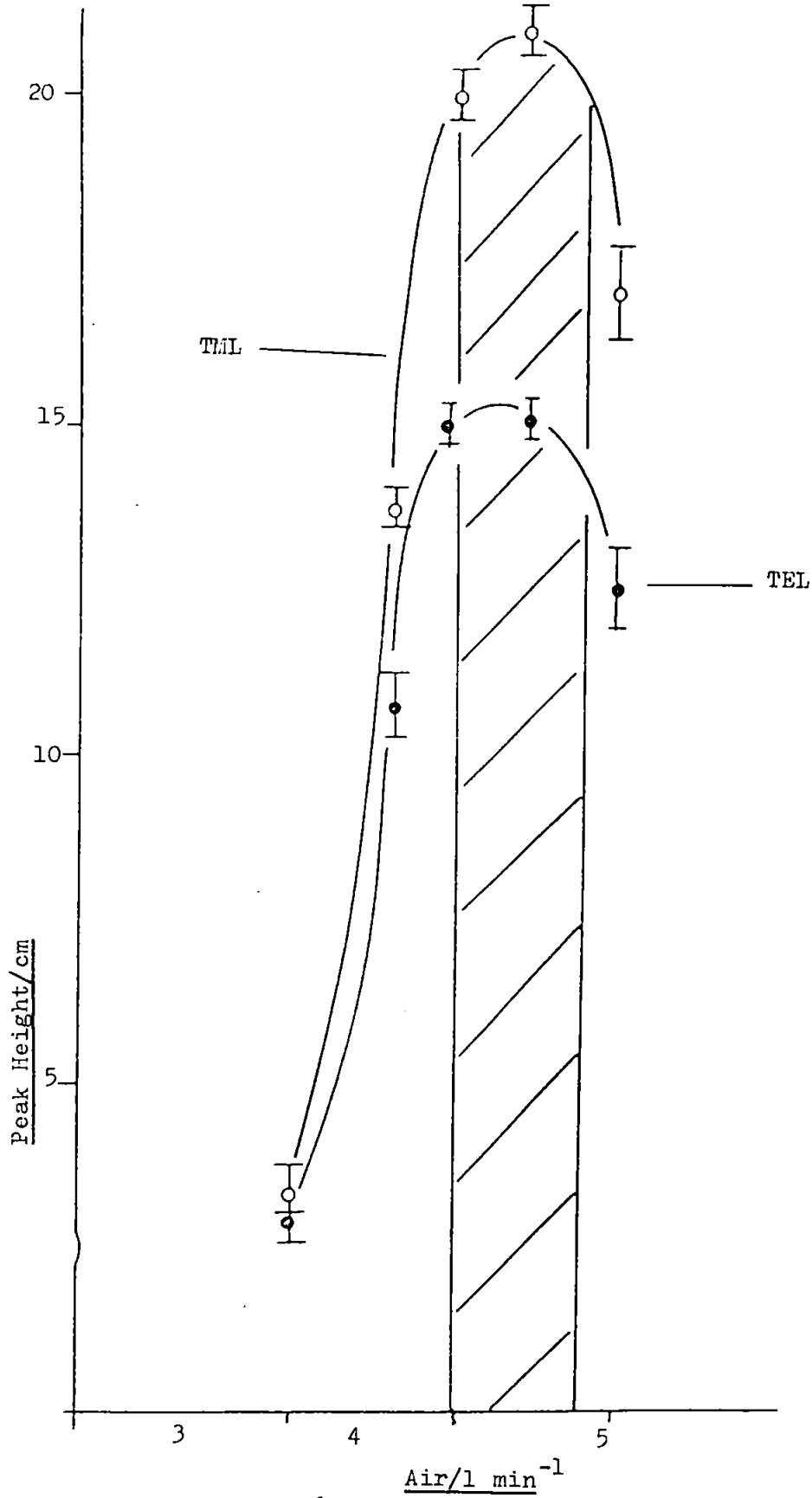


Figure 10(c)

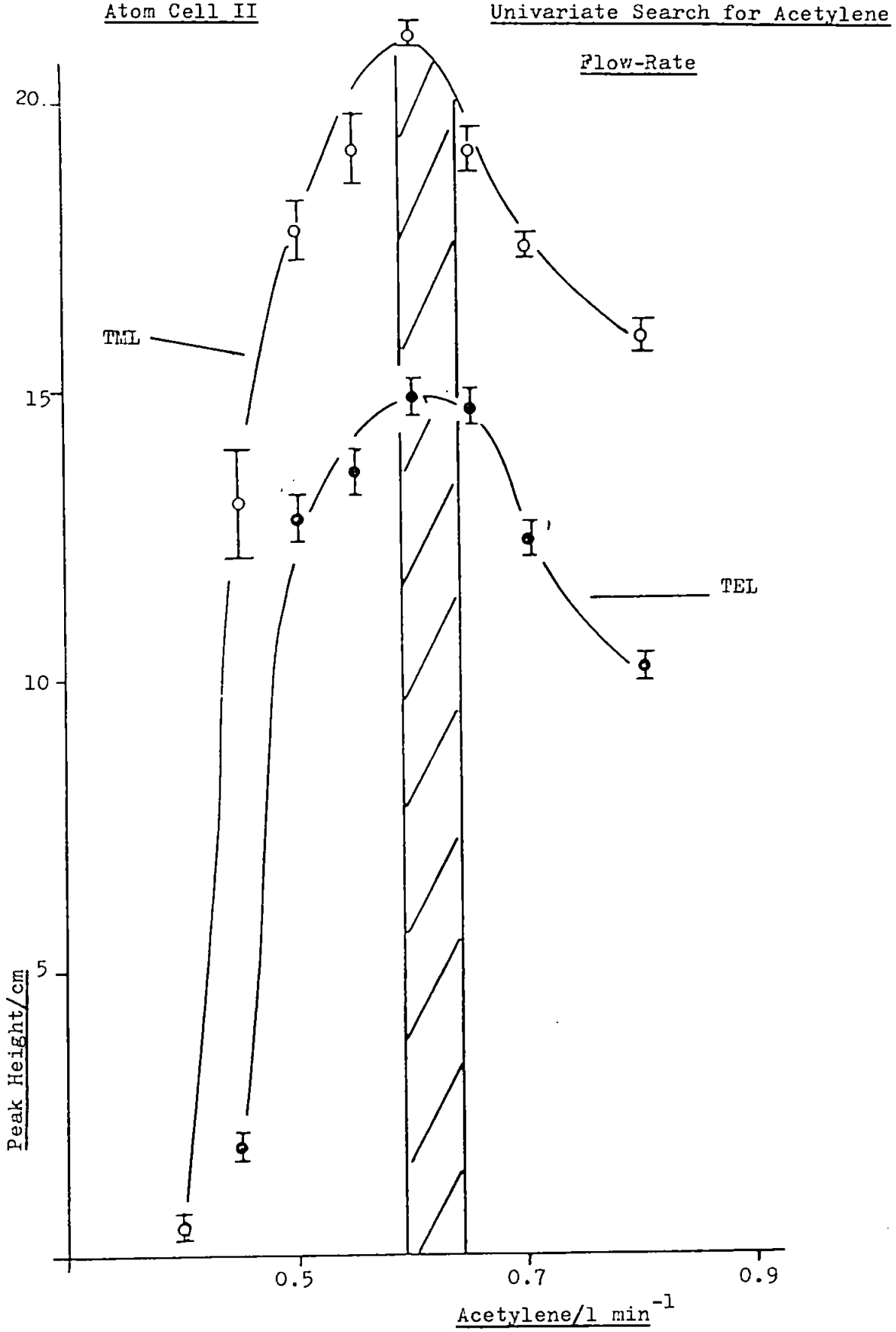

Atom Cell II
Univariate Search for Acetylene Flow-Rate
TML
TEL
20
15
10
5
Peak Height/cm
0.5
0.7
0.9
Acetylene/l min^{-1}

Figure 10(d)

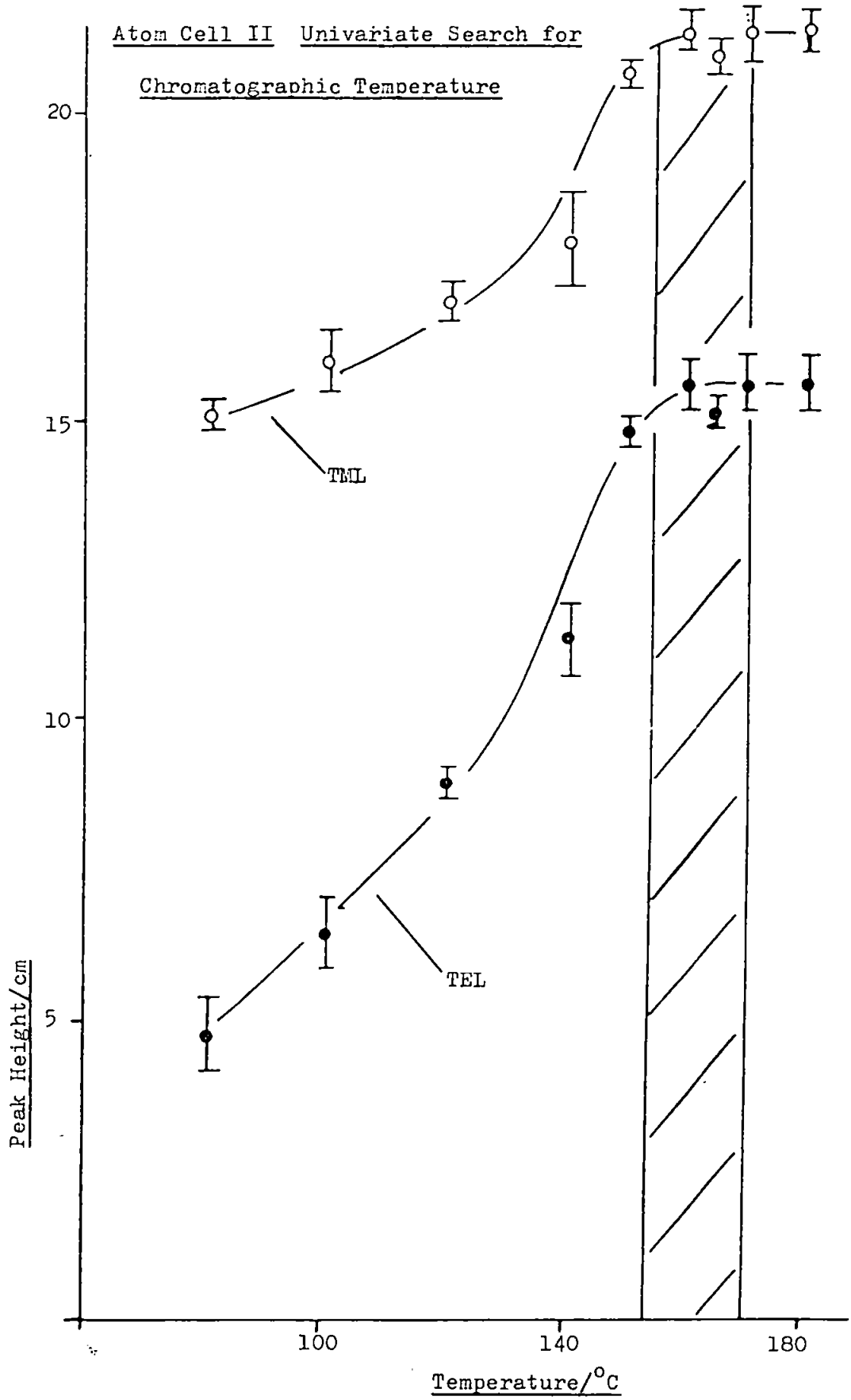
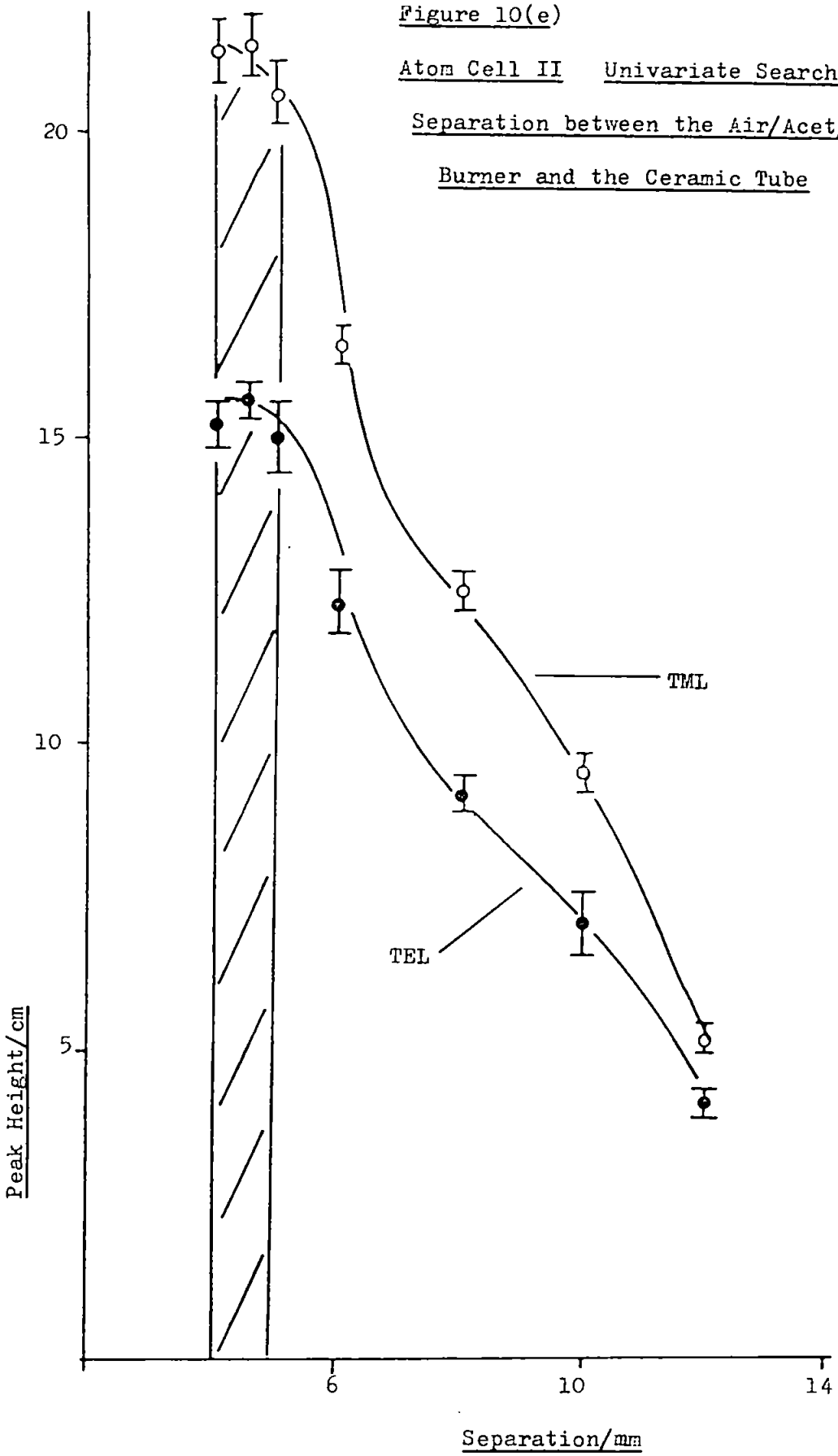

Atom Cell II Univariate Search for
Chromatographic Temperature
20
15
10
5
TML
TEL
Peak Height/cm
100
140
180
Temperature/°C

Figure 10(e)

Atom Cell II Univariate Search for the Separation between the Air/Acetylene Burner and the Ceramic Tube



depict the optimum range of values in the final simplex set. The carrier gas flow-rate, fig. 10(a), proved to be an extremely critical variable with a narrow optimum range. The lateral velocity of the carrier gas at the centroid was 1.46 m s^{-1}, which was just below the maximum burning velocity of the air/acetylene flame. As the lateral velocity increased above this value, the possibility of the nitrogen gas stream shooting straight through the flame, and thus not into the ceramic tube, increased. Obviously below this flow-rate, the possibility of eddy currents taking the analyte around the outside of the ceramic tube was increased. The univariate searches for the oxidant and fuel gas flow-rate, fig. 10(b) and (c), demonstrate both to be important variables with the optimum ranges being at those values which gave the most stoichiometric flame. The univariate search for the chromatographic column temperature, fig. 10(d), confirmed the conclusions made during the preceding optimisation. Fig. 10(e) demonstrates that the optimum ceramic tube - air/acetylene burner separation was the smallest possible that would allow a stable flame to be burnt. Minimisation of this separation obviously maximised the possibility of lead atoms entering through the hole in the ceramic tube.

5.3.3 Atom Cell III

The continuously variable parameters of this system were the same as for atom cell II. The centroid values of the simplex predicted optimum ranges are given in Table 12, column 3, with the univariate searches in Fig. 11(a) - (e). The optimum range for the nitrogen carrier gas flow-rate, fig. 11(a), was much higher than in the previous system. High nitrogen flow-rates will give a more laminar gas column, much less susceptible to directional fluctuations, hence giving the atoms a

Figure 11(a)

Atom Cell III Univariate Search for Nitrogen Flow-Rate

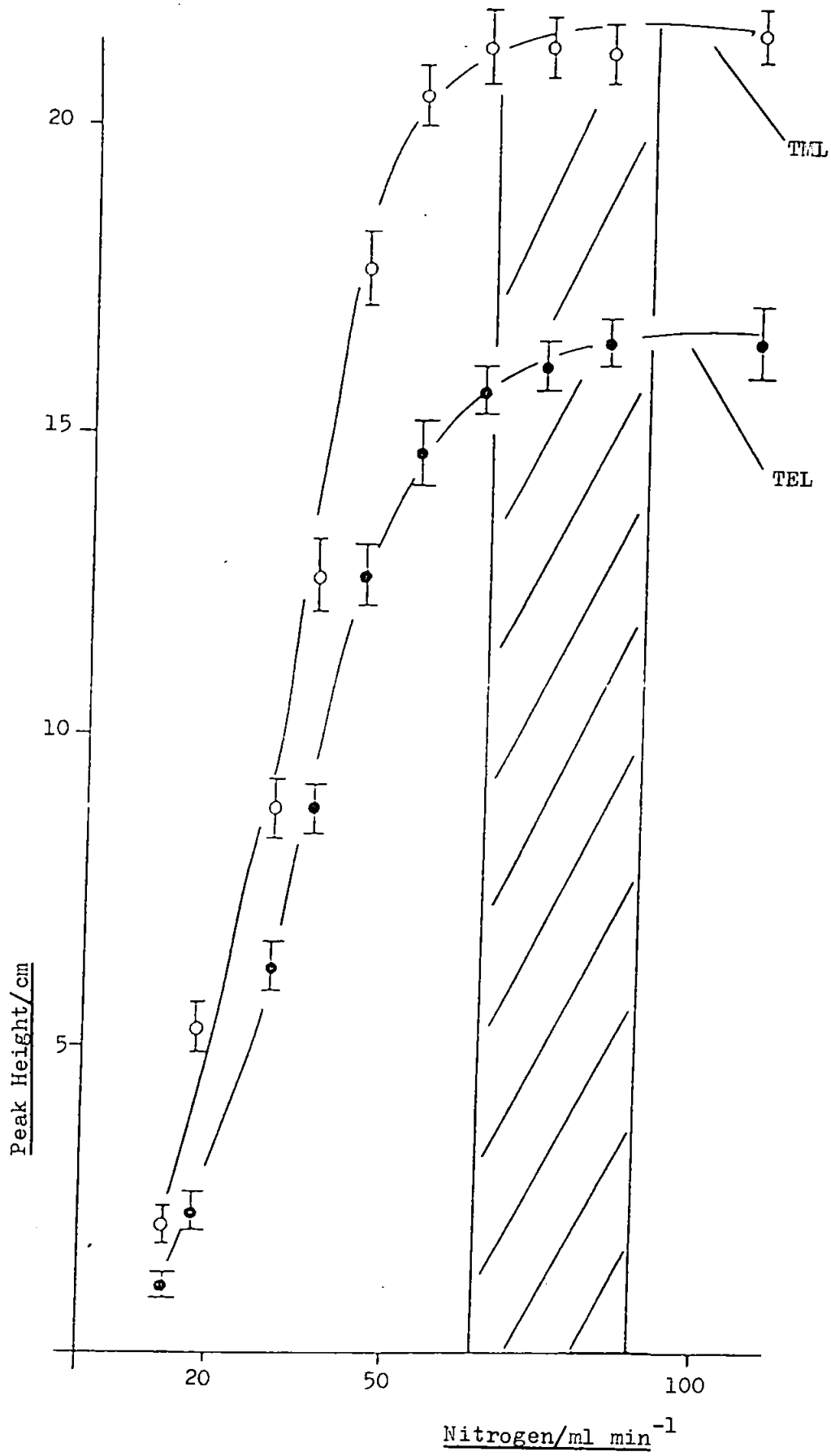


Figure 11(b)

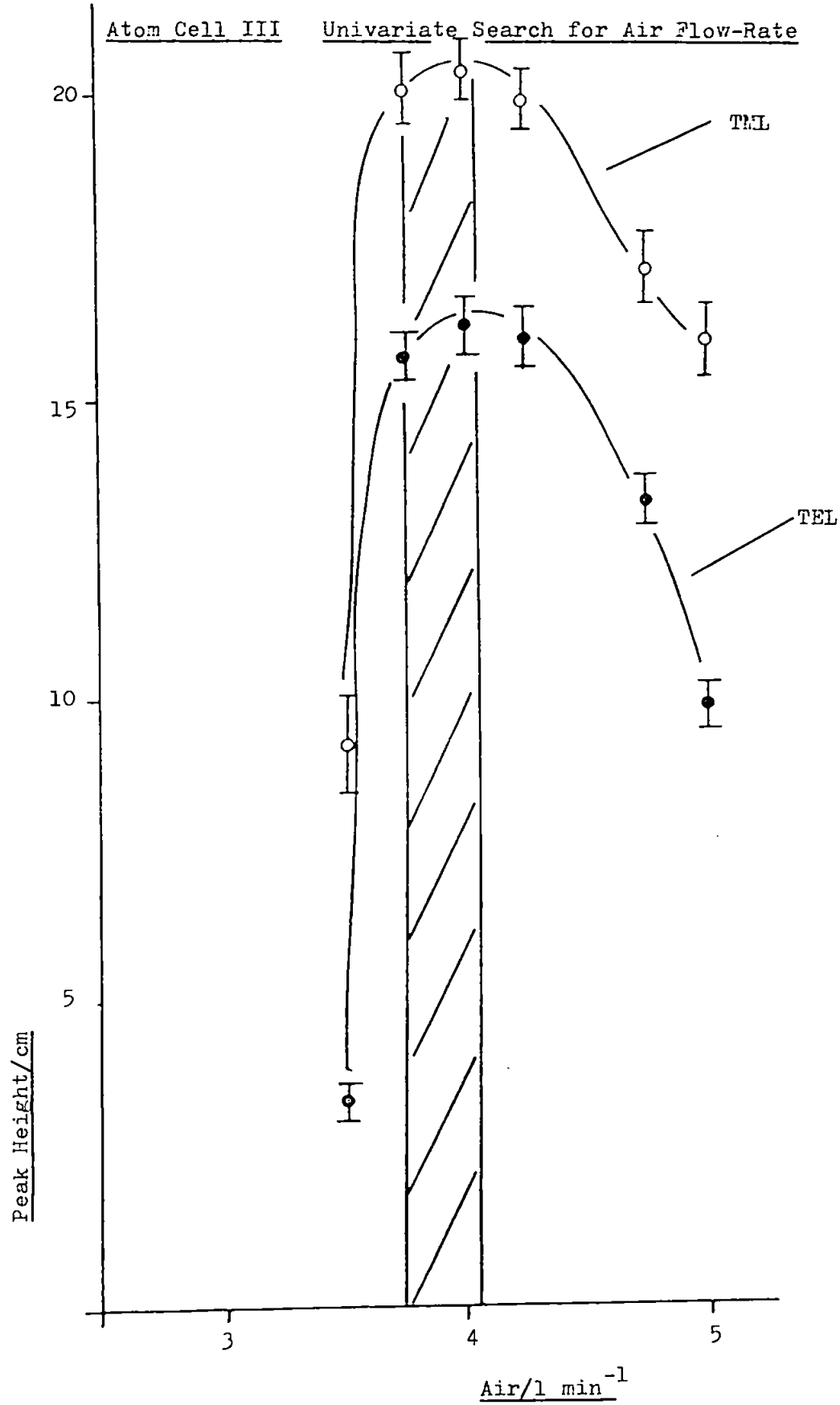

Atom Cell III
Univariate Search for Air Flow-Rate
TML
TEL
20
15
10
5
Peak Height/cm
3
4
5
Air/l min-1

Figure 11(c)

Atom Cell III Univariate Search for Acetylene Flow-Rate

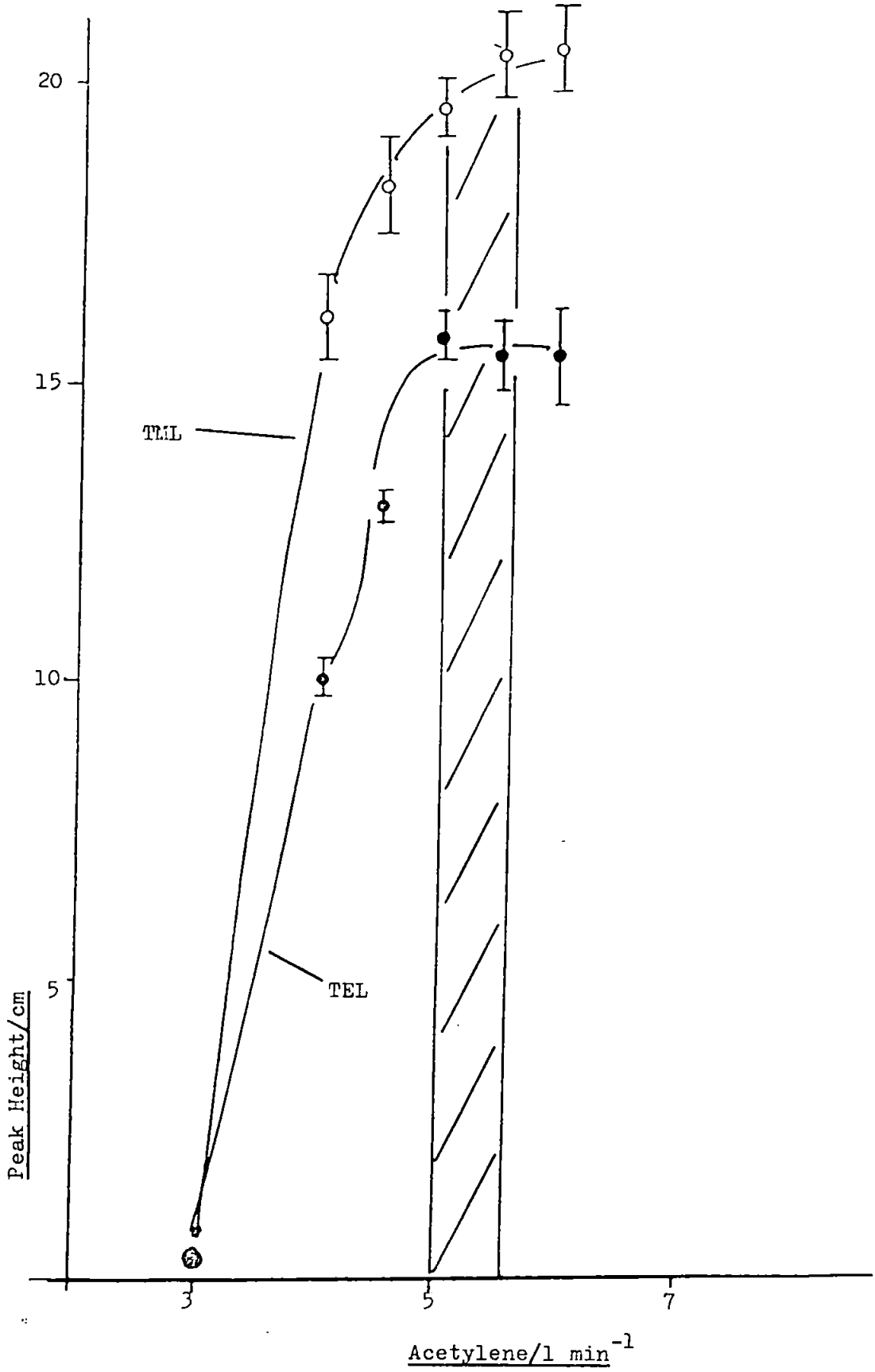


Figure 11(d)

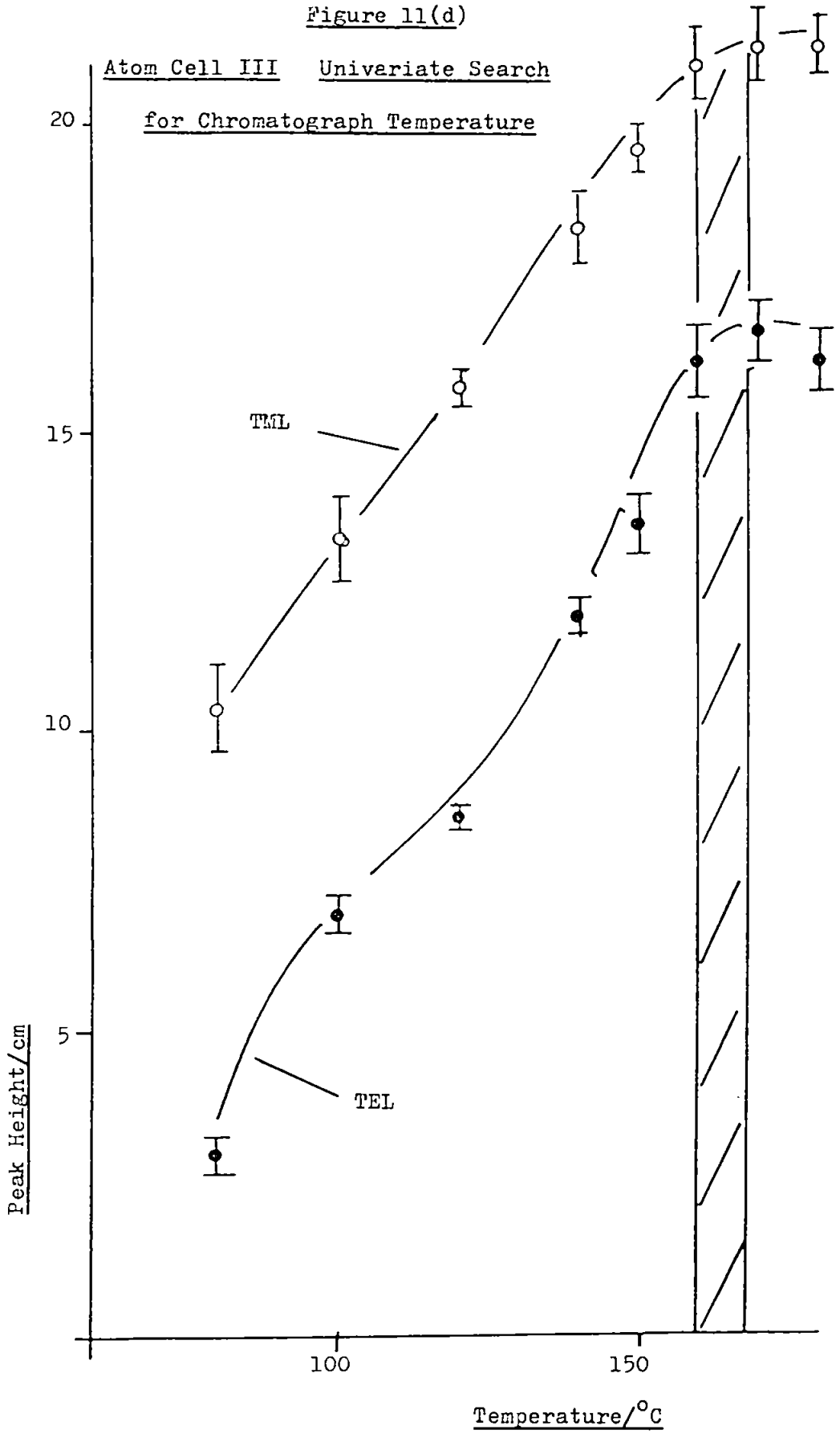
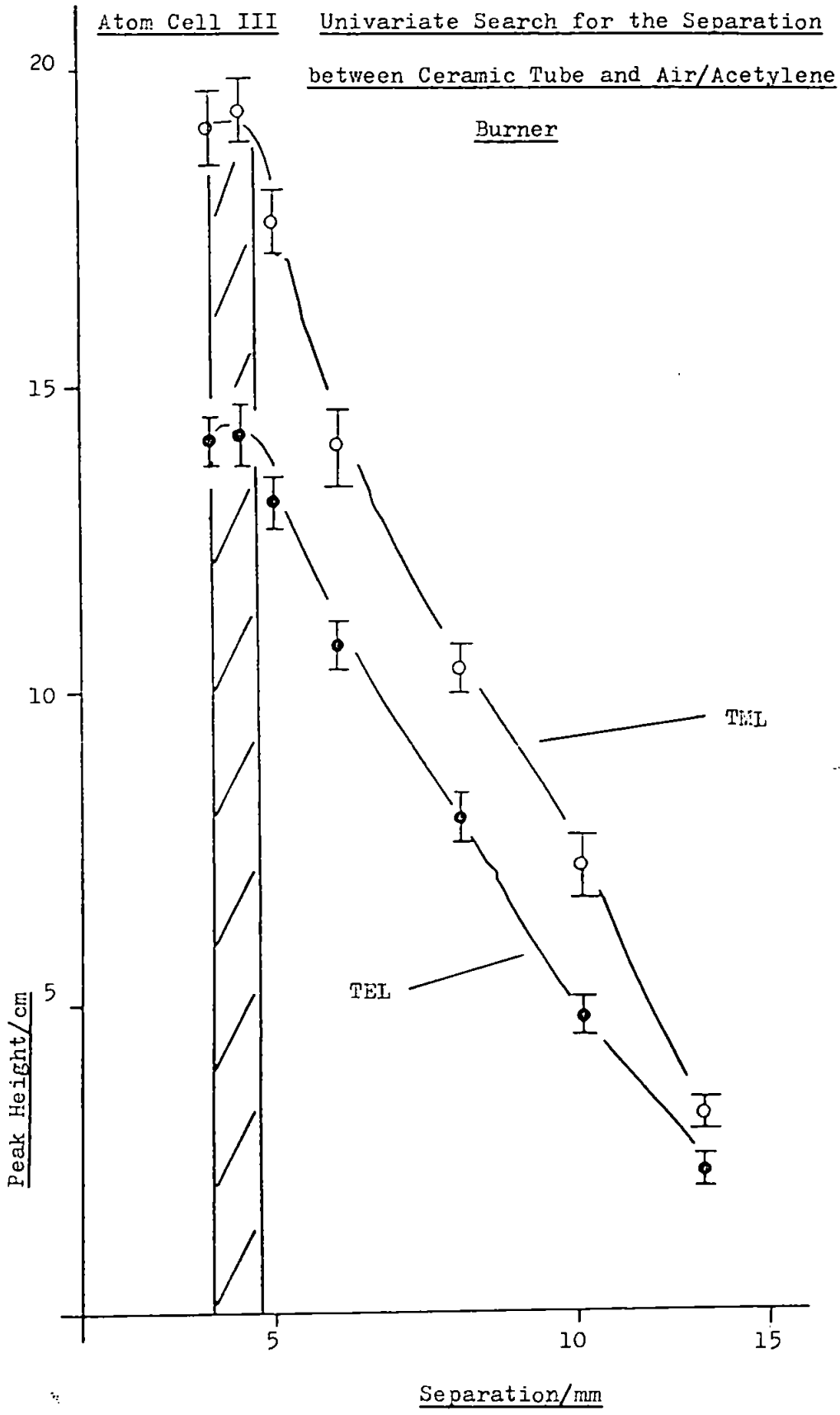

Atom Cell III Univeriate Search
for Chromatograph Temperature
20
15
10
5
TML
TEL
100
150
Peak Height/cm
Temperature/°C

Figure 11(e)


Atom Cell III
Univariate Search for the Separation between Ceramic Tube and Air/Acetylene Burner
20
15
10
5
Peak Height/cm
TML
TEL
5
10
15
Separation/mm

better chance of entering the ceramic tube. The slight advantage of atom cell III is presumably due to the increased control over the entry of atoms into the tube. Fig. 11(b) and (c) illustrate the critical nature of the oxidant and fuel gas flow-rates. The other optimum values were very similar to those observed for atom cell II, except a smaller flame was preferred because the flame no longer swept the atoms into the tube, and rather the role of the flame gases in sweeping out the tube was emphasised.

5.3.4 Atom Cell IV

The continuously variable parameters for this atom cell were the same as for atom cell II with the addition of the hydrogen flow-rate to the glass lined 'T' piece and the hydrogen diffusion flame burner - ceramic tube separation.

Fig. 12(a)-(g) illustrate the success of the simplex procedure. Fig. 12(a) shows that the nitrogen flow-rate was a critical parameter; it can be seen that the simplex found a flow-rate range which gives the best compromise peak height values for both TML and TEL. The apparent anomaly at low flow-rates for the TML may be related to the co-elution of the solvent mentioned earlier.

Fig. 12(b) and (c) illustrate again that the simplex has identified the optimum air and acetylene flow-rates as those consistent with a stoichiometric flame. Fig. 12(d) illustrates that the hydrogen flow-rate is the least critical of the gas flow-rates in this atom cell. Indeed, the major role of the hydrogen flame appeared to be to prevent the appearance of large solvent peaks, caused by uncorrected molecular

Figure 12(a)

Atom Cell IV Univariate Search for Nitrogen Flow-Rate

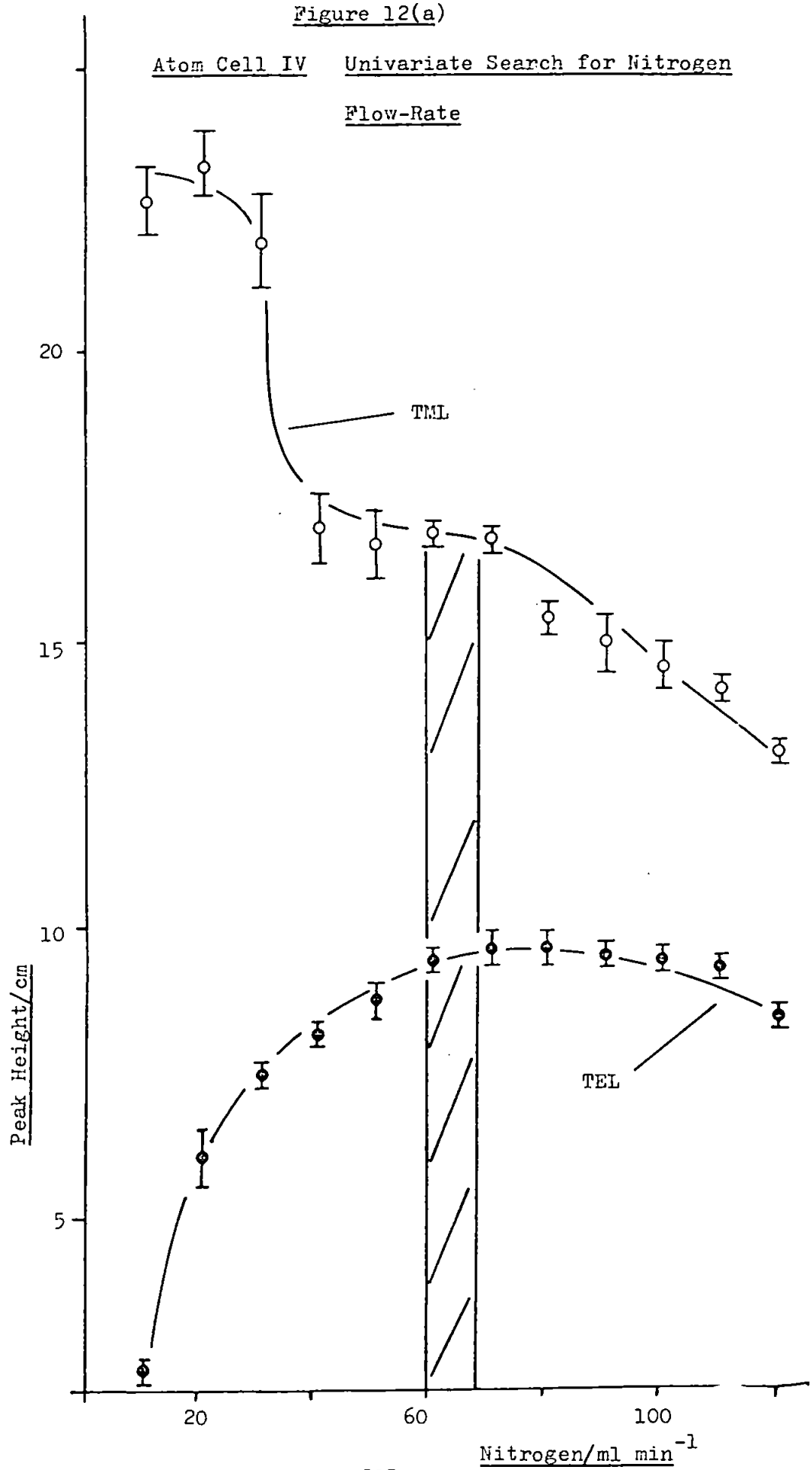


Figure 12(b)

Atom Cell IV

Univariate Search for Air Flow-Rate

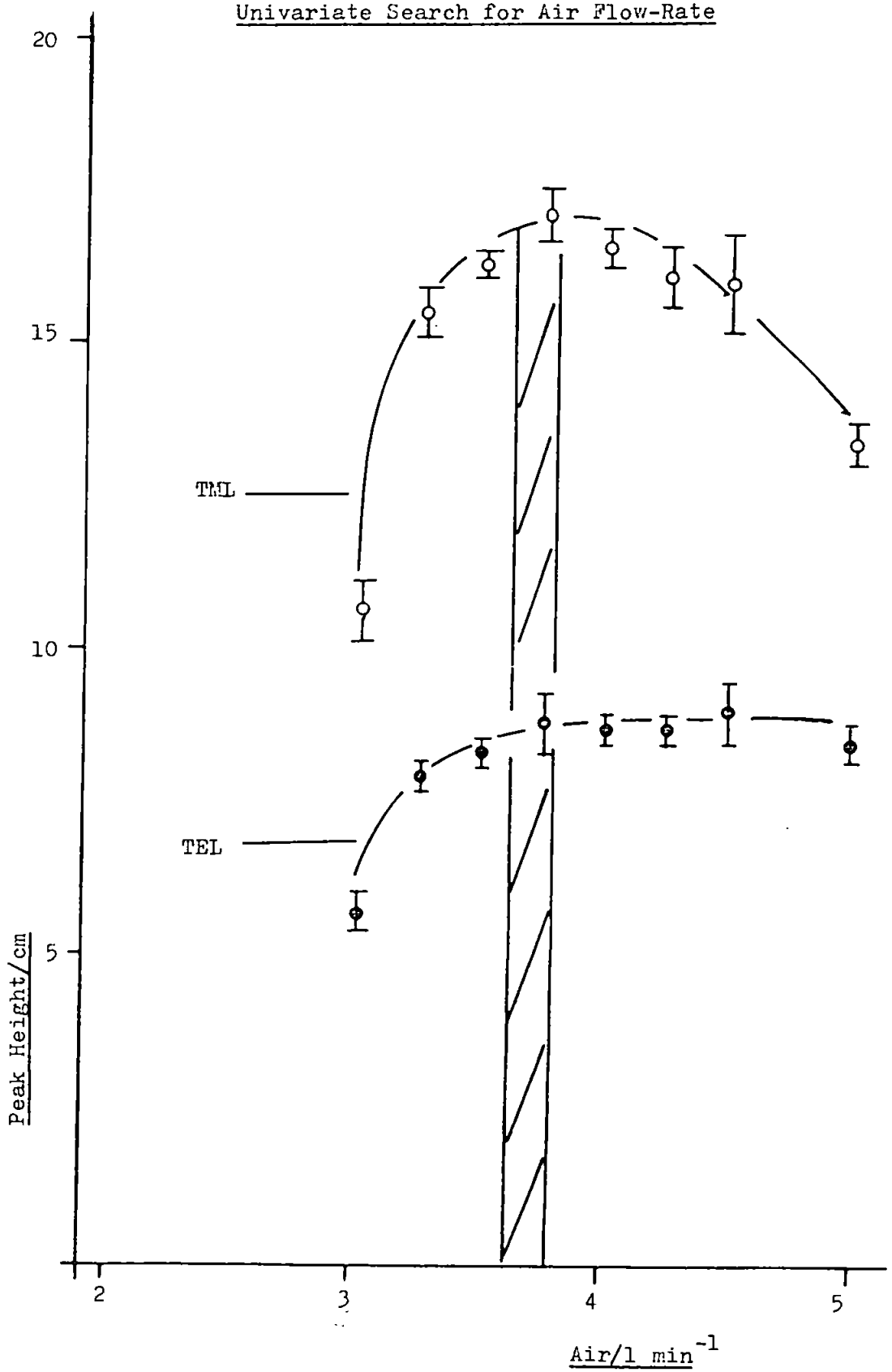


Figure 12(c)

Atom Cell IV

Univariate Search for Acetylene Flow-Rate

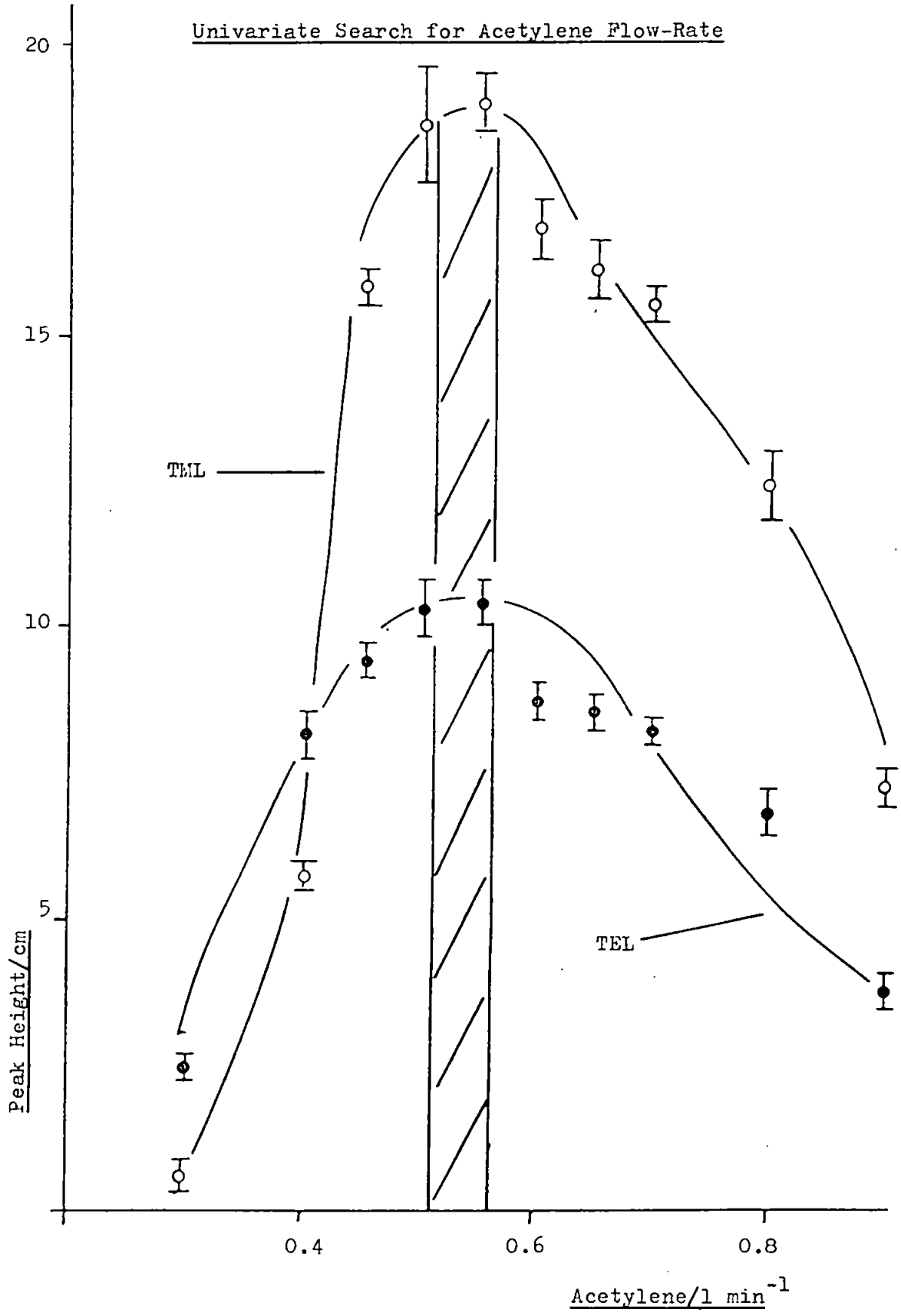


Figure 12(d)

Atom Cell IV

Univariate Search for Hydrogen Flow-Rate

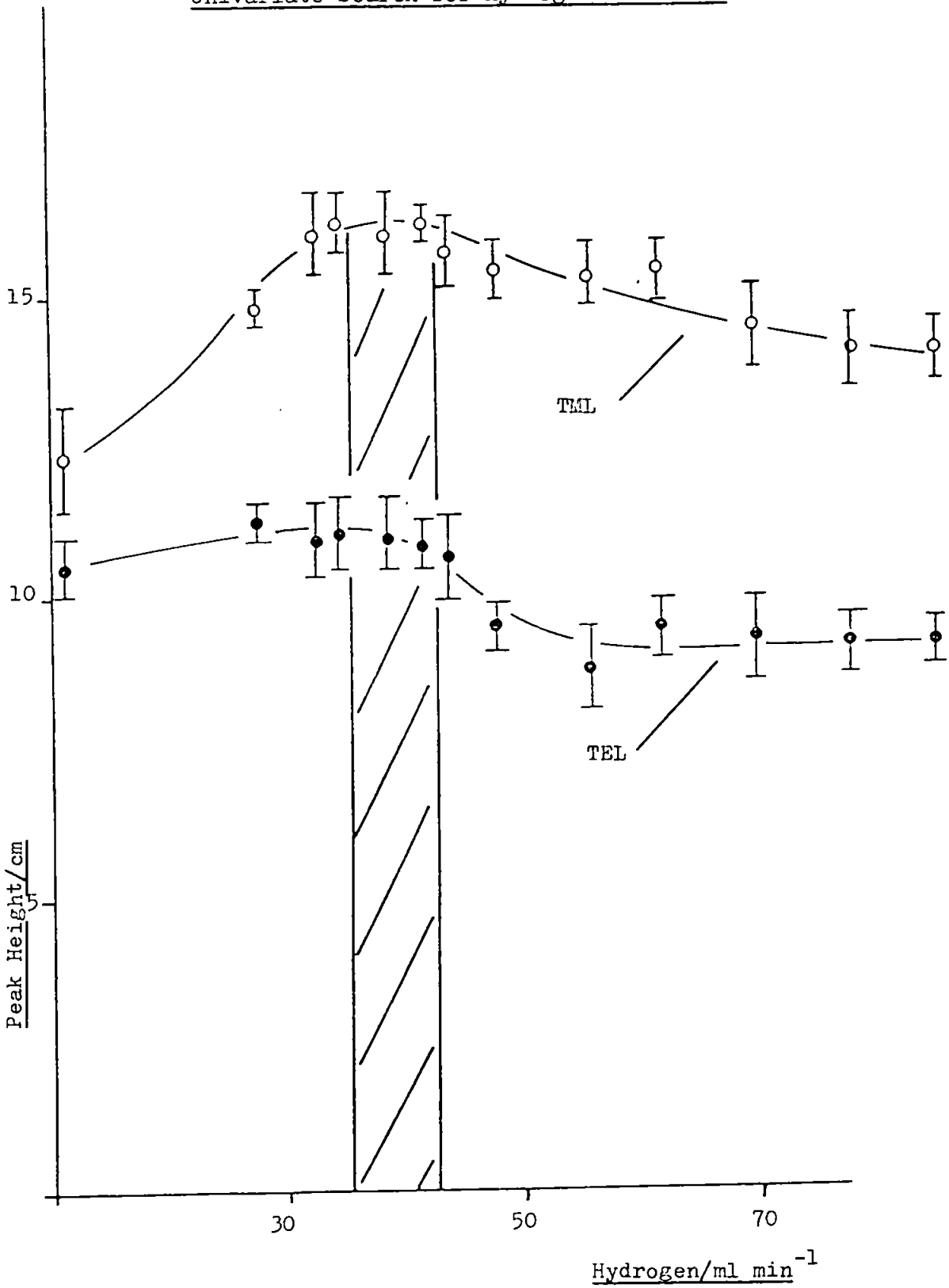


Figure 12(e)

Atom Cell IV

Univariate Search for Chromatographic Temperature

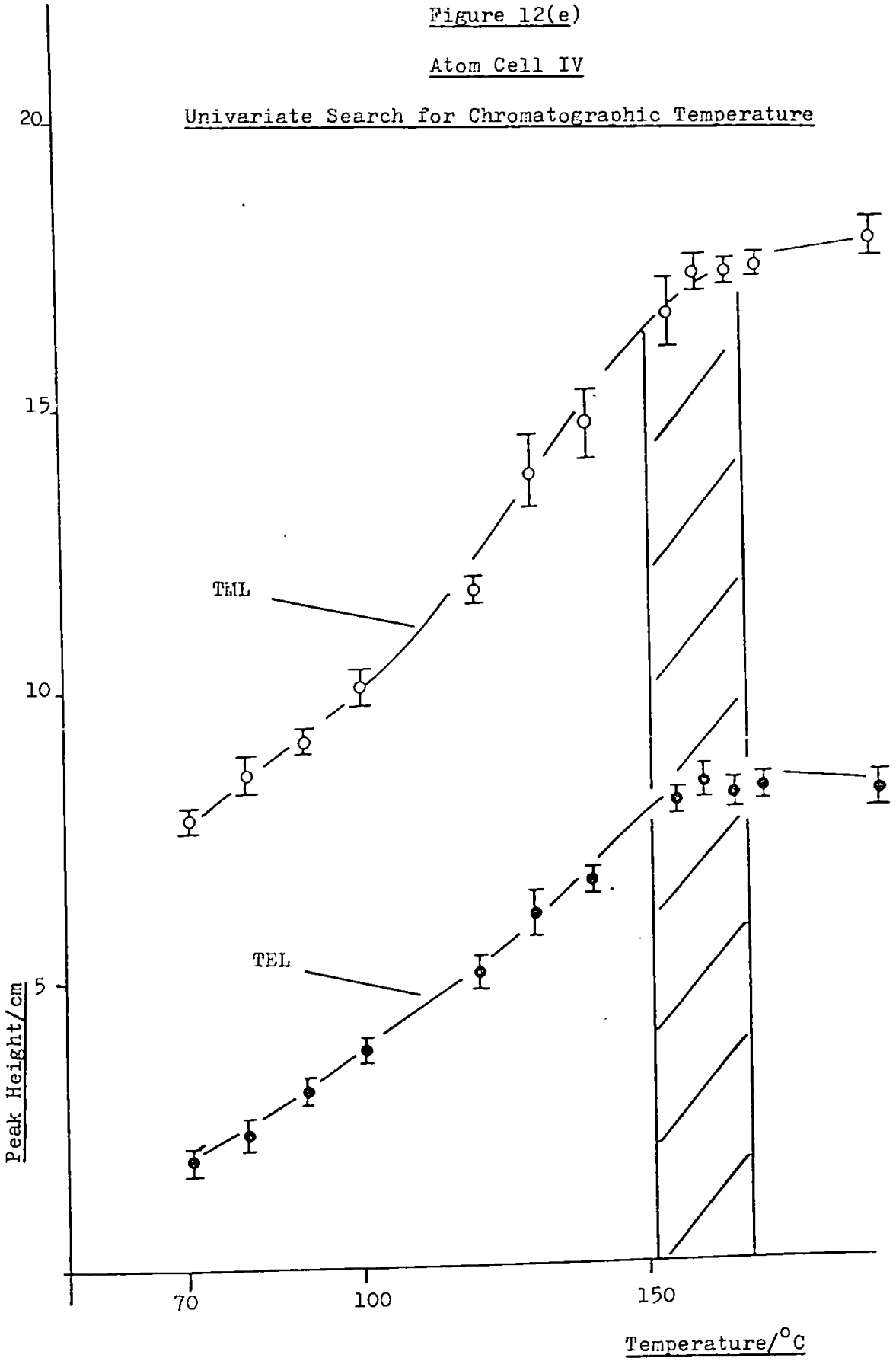


Figure 12(f)

Atom Cell IV

Univariate Search for Separation between Ceramic Tube and Air/Acetylene Burner

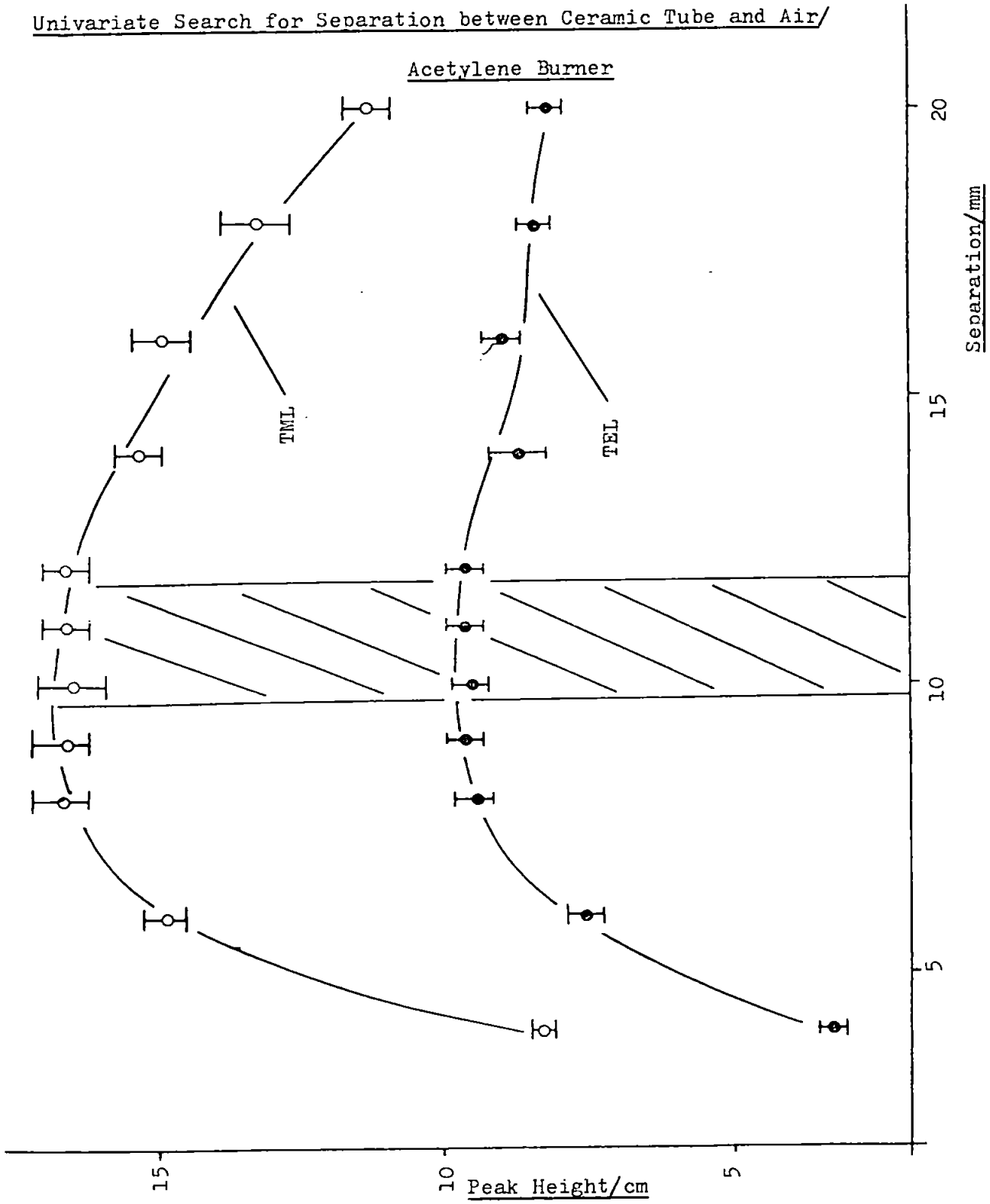
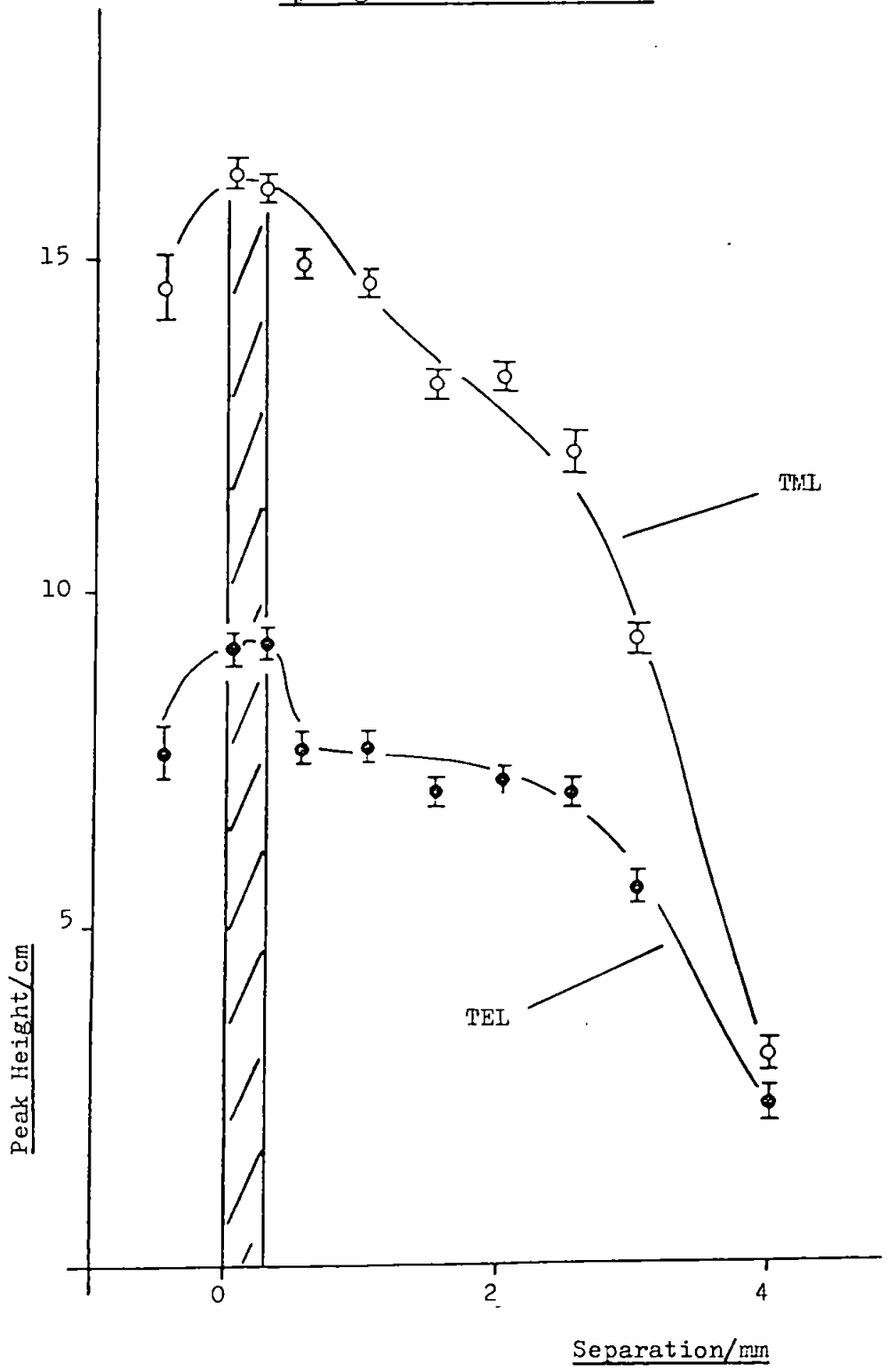


Figure 12(g)

Atom Cell IV

Univariate Search for Separation between the Ceramic Tube and the Hydrogen Diffusion Burner



absorption, and to aid the formation of reproducible narrow peaks. This effect is illustrated in fig. 13(a) and (b), where 'I' shows the point of sample injection. Fig. 12(f) shows that the predicted optimum range for the ceramic tube air/acetylene occupied only part of the optimum range as shown by the univariate search. The occurrence of a wide optimum range makes it difficult, though not critical, to identify closely the optimum range. This separation was much greater than for the previous two atom cells and this reflects the fact that the function of the air/acetylene flame is just to heat the ceramic tube and plays no part in the transport of atoms into the tube. Fig. 12(g) indicates that the separation between the ceramic tube and the hydrogen burner is a critical parameter. It is understandable that as the separation increased, the response to lead, for both TML and TEL, decreased because of the increased chance of effluent not entering the ceramic tube through the hole, but rather being swept around the tube by the air/acetylene flame. The fact that the lead response was decreased if the hydrogen diffusion burner was placed inside the ceramic tube (defined as a negative separation on the figure) suggests that the air/acetylene flame was not merely heating the ceramic tube. It appears that this flame also played a part in ensuring that the hydrogen flame remained burning so as to give efficient atomisation.

5.3.5 Atom Cell V

The continuously variable parameters investigated for this system were nitrogen carrier gas, chromatographic temperature, hydrogen flow-rate to the glass-lined 'T' piece and the ceramic tube temperature. The optimum range predicted by the simplex optimisation is given for each variable in Table 13. Figures 14(a)-(d) demonstrate the success of the

Figure 13(a)

Chromatograms Obtained with Atom Cell IV Under Optimum Conditions

(i) Injection of 1.0μl of 2,2,4 - trimethylpentane

(ii) Injection of 1.0μl of TML (1 mg l^{-1}) and TEL (1 mg l^{-1}) in 2,2,4 - trimethylpentane

I = point of injection

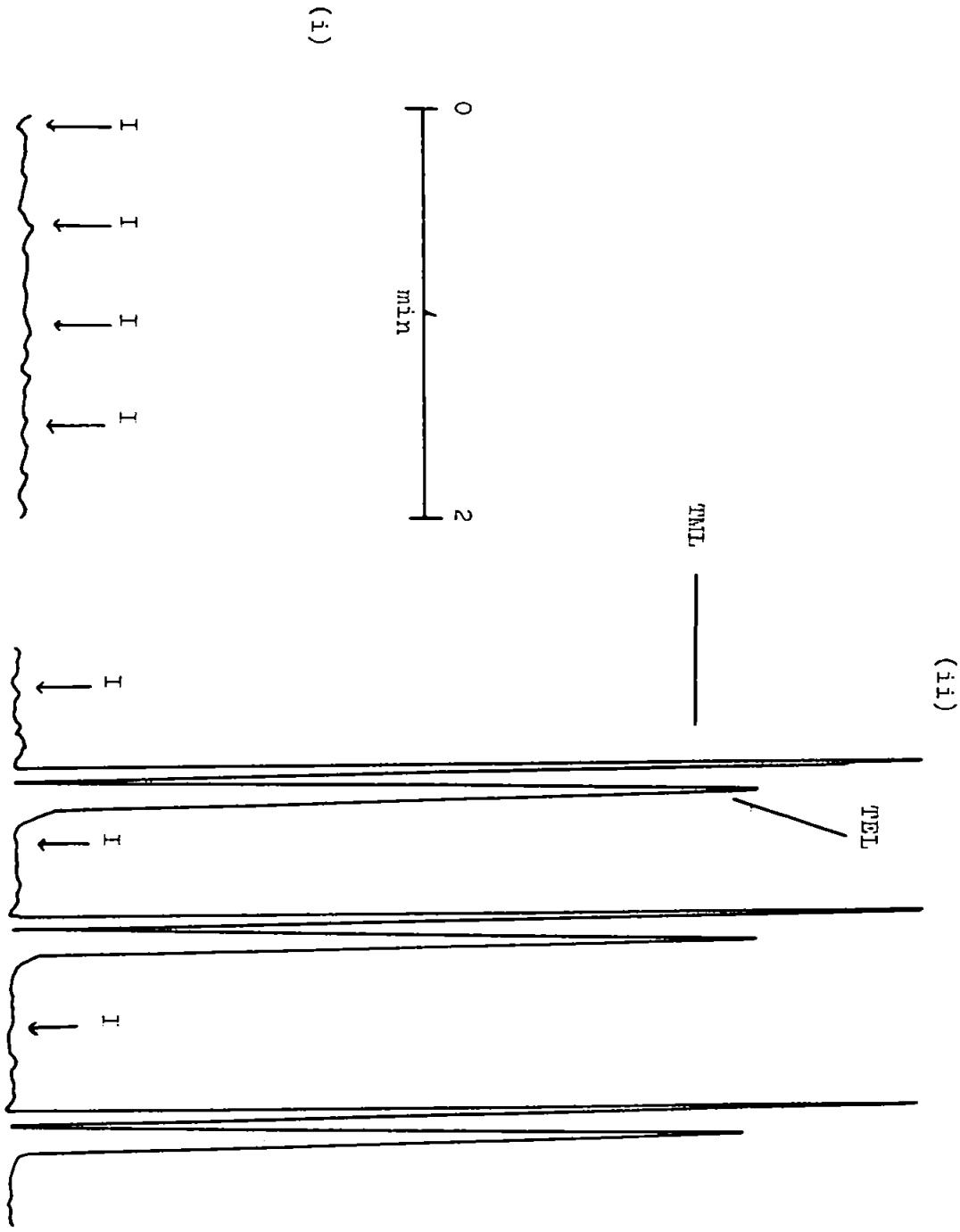


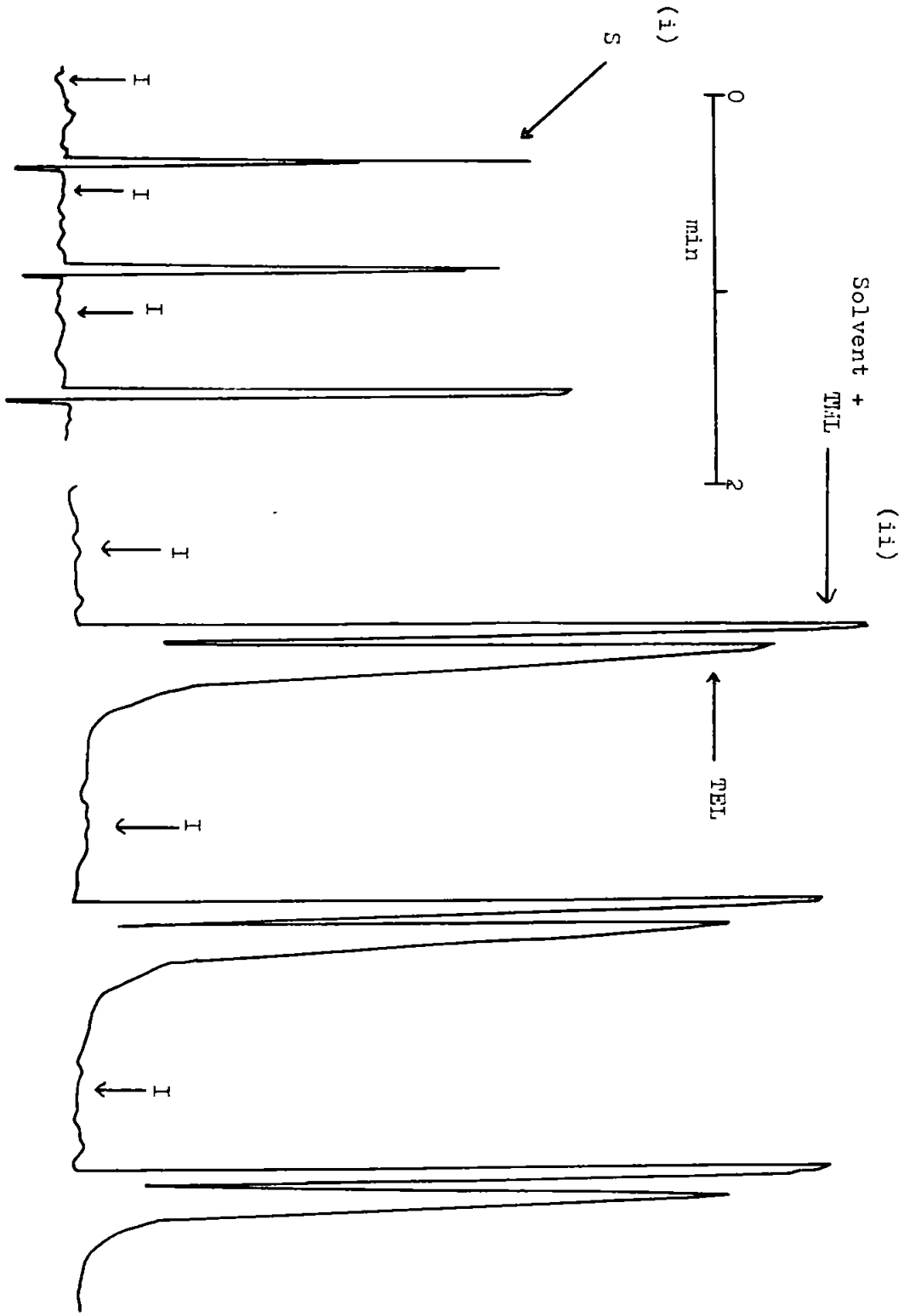
Figure 13(b)

Chromatograms Obtained with Atom Cell IV with Zero Hydrogen Flow-Rate

(i) Injection of 1.0μl 2,2,4 - trimethylpentane

(ii) Injection of 1.0μl TML (1.0 mg l^{-1}) and TEL (1.0 mg l^{-1}) in 2,2,4 - trimethylpentane

I = point of injection



optimisation procedure and the shaded region on each graph identifies the optimum range predicted.

The optimum range for the carrier gas flow, fig. 14(a), is lower than that found for atom cell IV, which probably reflects the fact that in the electrothermally heated cell there are no flame gases flowing around the tube, which may restrict the entrance of the effluent through the hole in the tube. Since the carrier gas flow-rate is lower, the optimum chromatographic column temperature, fig. 14(c), is higher. Fig. 14(b) illustrates the success of the simplex in finding the optimum hydrogen flow-rate to the diffusion flame burner. The response surface for the hydrogen flow-rate is similar in shape to that for atom cell IV, fig. 12(d), but the response to lead is lower at low hydrogen flow-rates in atom cell V. The optimum range for atom cell V is also significantly higher than that for atom cell IV. This probably reflects the fact that in atom cell IV, the hydrogen flame is surrounded by the air/acetylene flame which can thus supply energy to the atomization process. This is obviously not the case in atom cell V, and this extra energy must be supplied by a larger flow of hydrogen to the diffusion flame. Fig. 14(d) illustrates the response curves for ceramic tube temperature and again shows the success of the simplex. The response curves for both TML and TEL are very similar, which is commensurate with the function of the heated tube, i.e. prevention of condensation of the atomic species after atomization in the hydrogen flame. Optical comparison of the ceramic tube showed its temperature when flame or electrothermally heated to be similar.

Table 13

Centroid Values Obtained for the Simplex Variables in Atom Cell V

Variable	Centroid Value
Nitrogen flow rate / ml min^{-1}	40
Hydrogen flow rate / ml min^{-1}	70
Chromatographic column temperature / ^{o}C	180
Ceramic tube temperature / ^{o}C	1040

Figure 14(a)

Atom Cell V

Univariate Search for Nitrogen Flow-Rate

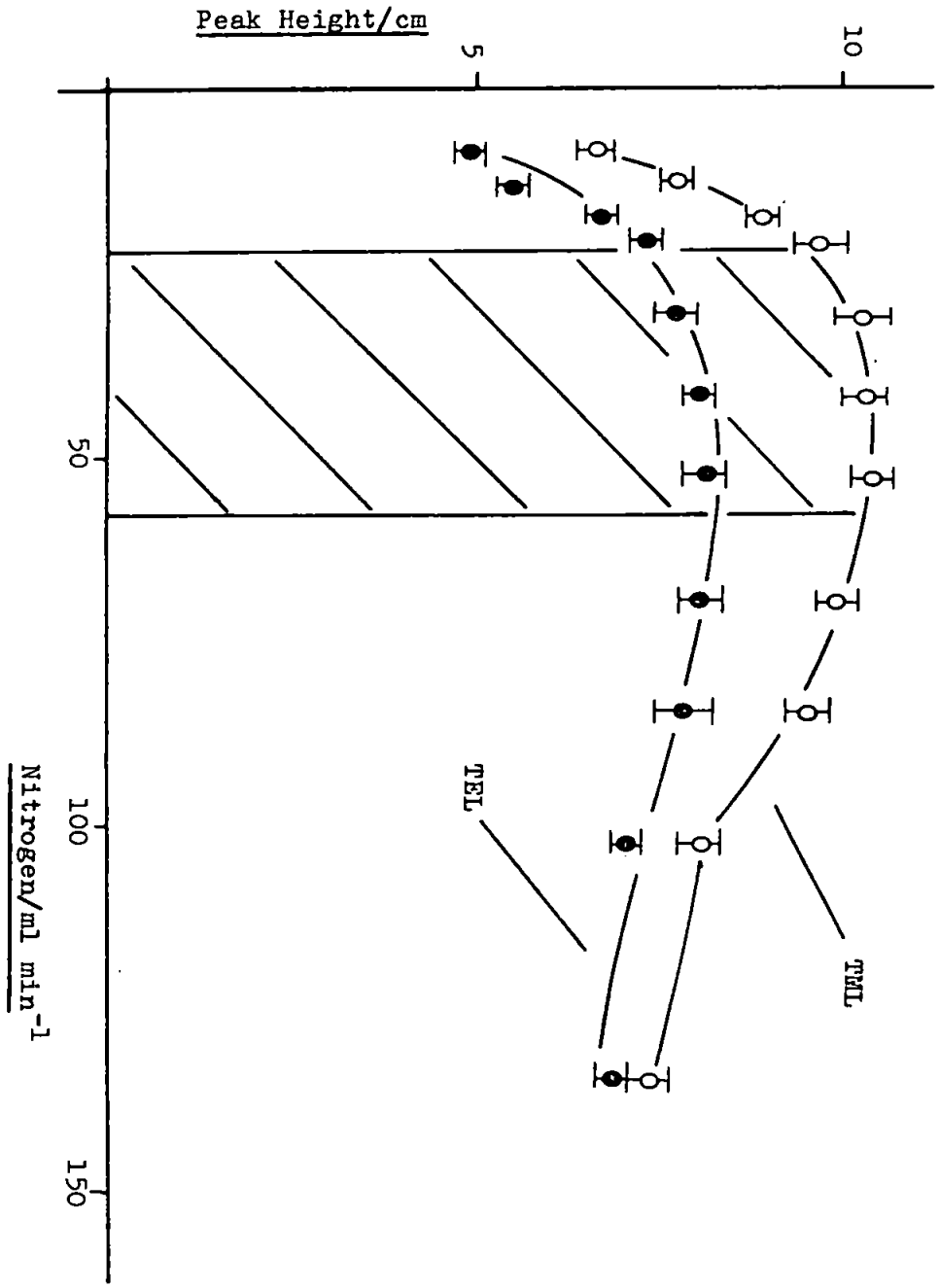


Figure 14(b)

Atom Cell V

Univariate Search for Hydrogen Flow Rate

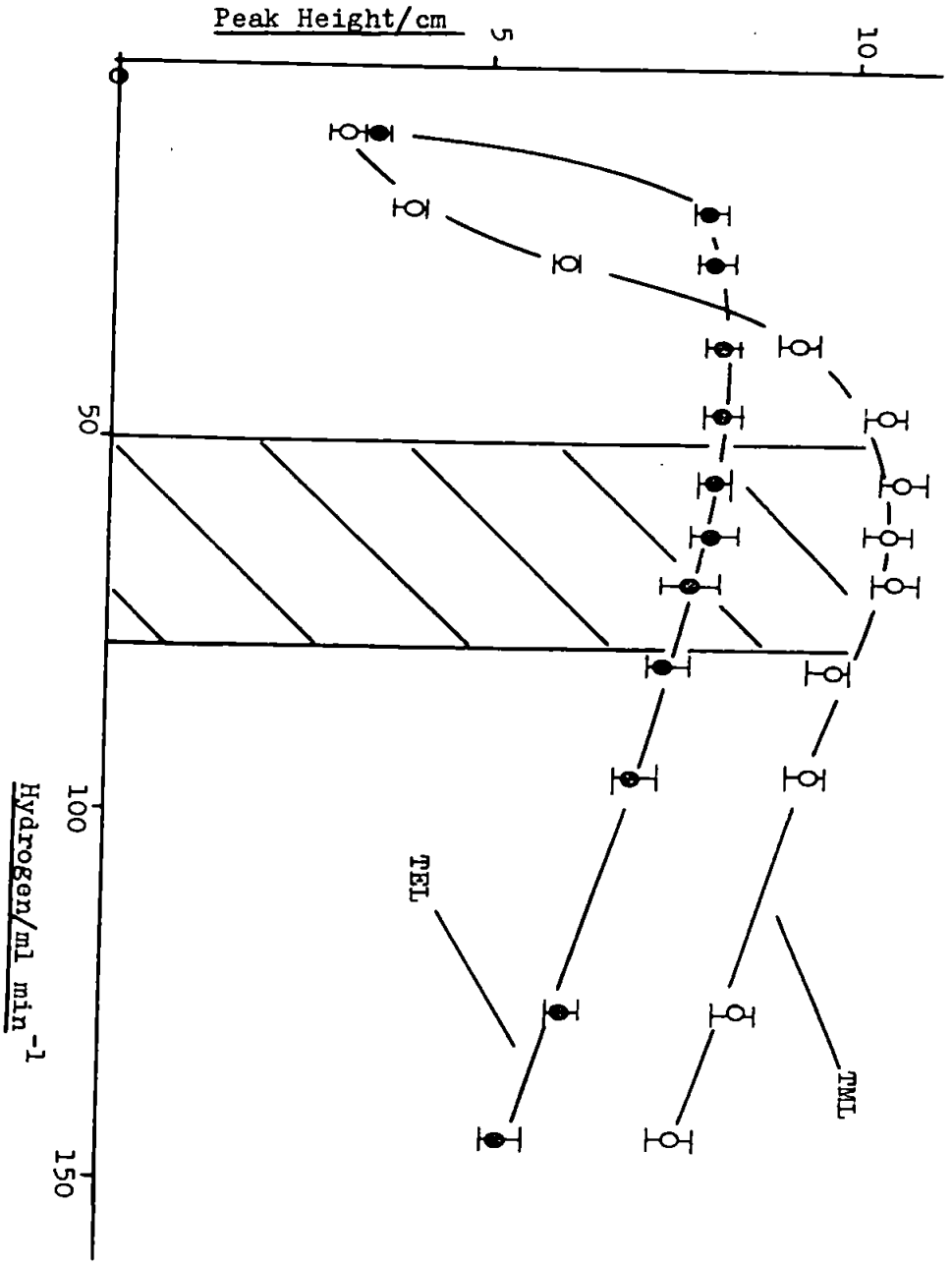


Figure 14(c)

Atom Cell V

Univariate Search for Chromatographic Temperature

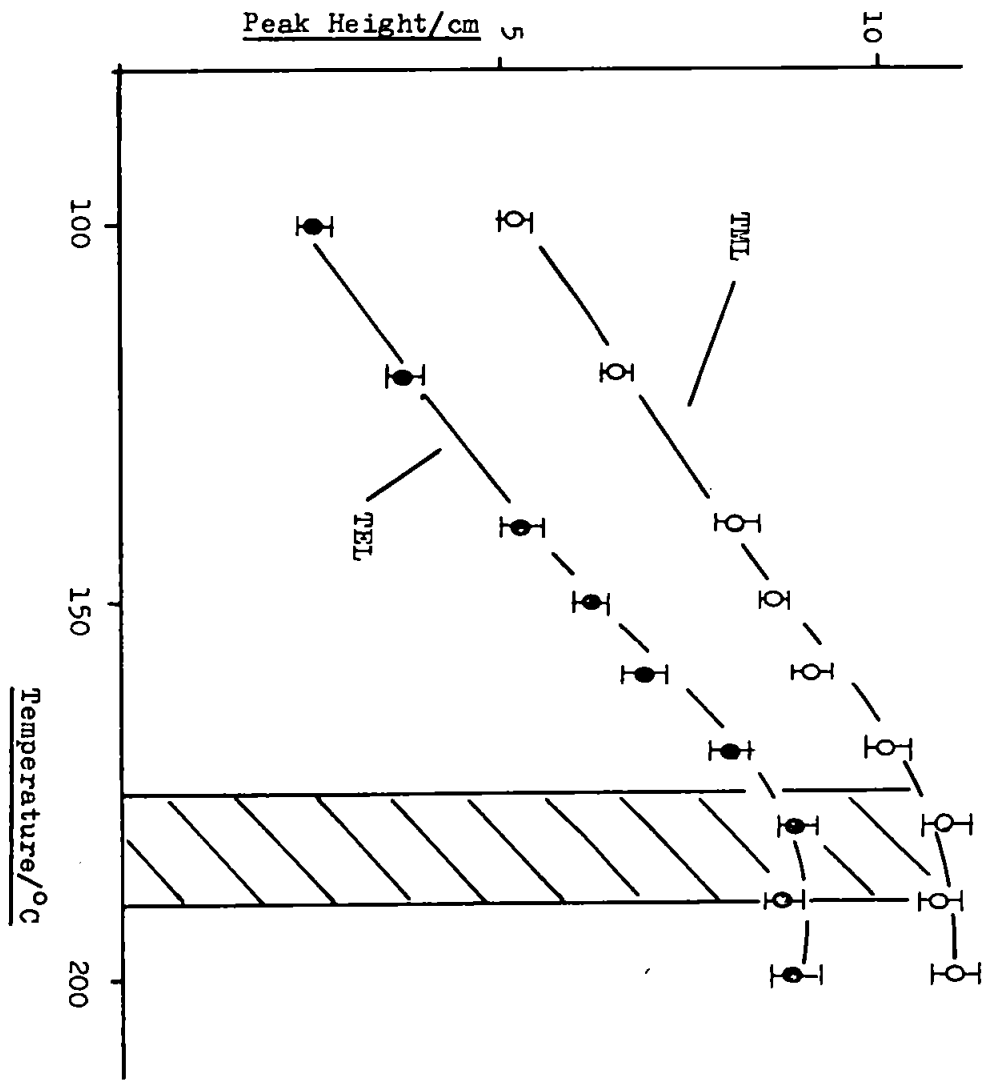
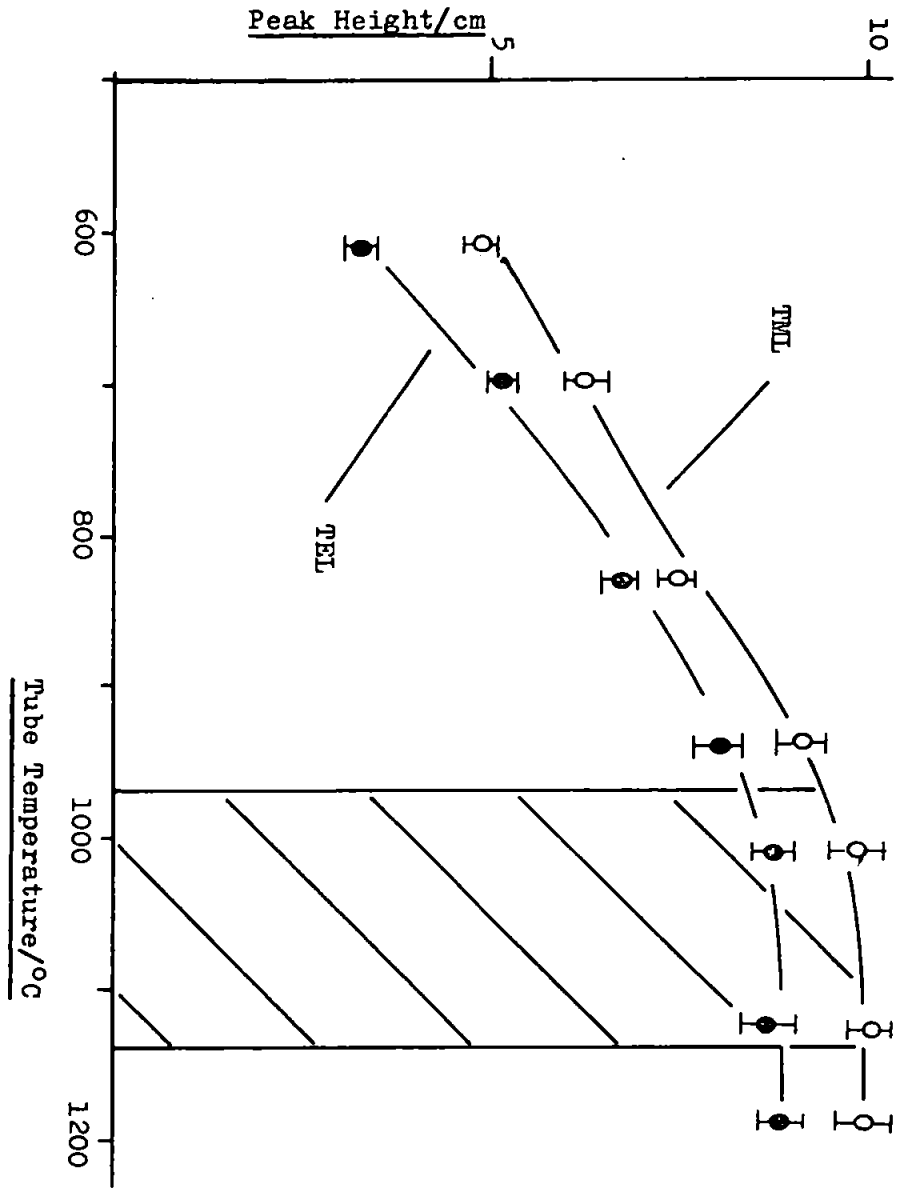


Figure 14(d)

Atom Cell V

Univariate Search for Ceramic Tube Temperature



5.3.6 Detection Limits and Linear Working Range

In atomic spectroscopy, detection limits generally quoted in the literature are based on the equation:

$$X_L = 2 S_B$$

where X_L is the limit of detection and S_B the standard deviation of the blank.

The use of a chromatographic technique gives the advantage that from retention times of the species a signal may be expected at a certain time after injection of sample. Thus, for this coupled GC-AAS technique, it would seem reasonable to measure the background variation at the retention time of the chromatographic peak. The retention times for both TML and TEL achieved with the five atom cells are given in Table 14. As an example of this method, Fig. 15 shows traces obtained using atom cell I for 10, 5, 4 and 3 ng of lead injected as TML and TEL. This atom cell gave detection limits of 1.0 and 2.0 ng for TML and TEL, respectively.

The detection limits for the five atom cells are given in Table 15. The introduction of the ceramic tube above the air/acetylene flame had a profound influence on the sensitivity of the detector. The separation of the atomisation process and heating of the ceramic tube functions, in atom cell IV, gave a further increase in response to lead. Both increases in response were caused by increasing the residence time of the atoms in the atom cell. The linear working ranges of each atom cell illustrate the drawback of any absorption technique, namely short linearity, however, by simply removing the ceramic tube the linear range obtainable may be extended.

Table 14

Retention Times Obtained for each Atom Cell Under Optimum Conditions

Atom Cell	Retention Time/s	
	TML	TEL
I	44	64
II	31	50
III	16	26
IV	26	34
V	32	53

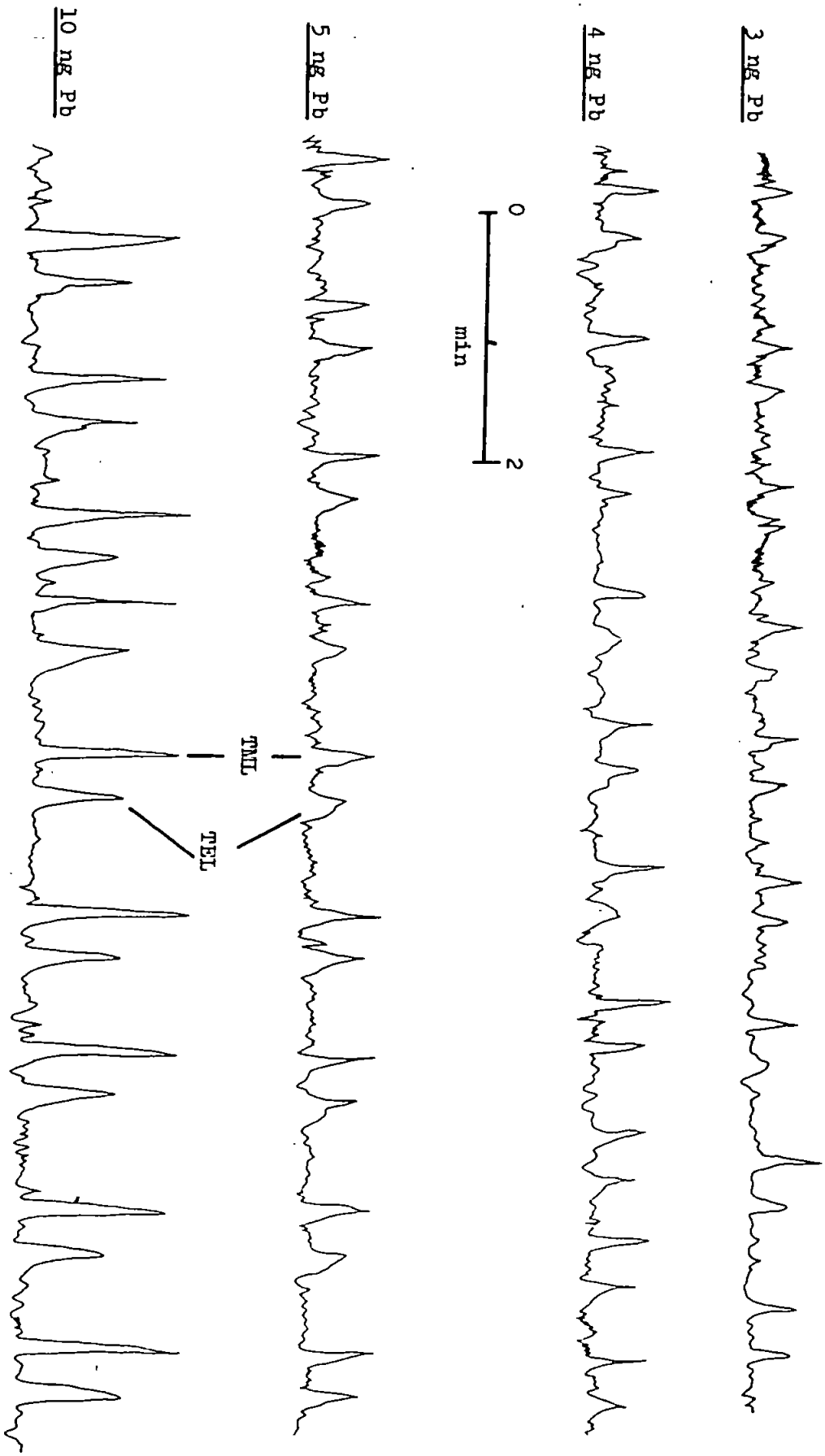
Table 15

Linear Working Range and Detection Limits (as Lead) for the Five Atom Cells

Atom Cell	Linear Range/ng	Detection Limit/pg	
		TML	TEL
I	10 - 300	1000	2000
II	1.0 - 50	58	75
III	0.8 - 20	48	71
IV	0.1 - 15	17	17
V	0.1 - 13	9	10

Figure 15

Chromatograms of Tetramethyllead and Tetraethyllead near the Detection Limit using Atom Cell I



5.4 CONCLUSION

The use of a flame atom cell as an atomic-absorption detector has the advantages of simple and well understood operation, and its continuous mode of operation is ideal for dealing with a continuous sample stream. The use of the ceramic tube device above the flame increased atom residence times so that the detection limits obtained were better even than the best reported for graphite furnace systems (199, 200). This shows that by paying attention to the atomic residence time within a flame, low levels of detection are possible. The fact that better detection limits are obtained shows that the residence times in atom cells IV and V are longer than in the furnace system of De Jonghe *et al*. (199, 200). The advantage of the atom cells developed over graphite furnaces is that they are designed for continuous heating which graphite furnaces are not.

As the height of the ceramic tube above the air/acetylene flame is now known, the atom cells may be further simplified by using either a knife edge support, plate 1, in conjunction with the SP 192 spectrometer or a cradle support, plate 2, in conjunction with the SP 9 spectrometer, which are readily demountable to permit rapid decoupling of the instruments. The experimental arrangement is illustrated in plate 3, which shows the coupling of the chromatograph with an SP 9 spectrometer. The electrothermally heated ceramic tube offers only marginal advantage in detectability over atom cell IV, but at a cost in simplicity and robustness of design. For the tube-in-flame detector, no additional heating is required in contrast to the electrothermally heated tube. Useful tube life times in excess of six months have been noted and observable memory effects are absent.

Plate 1

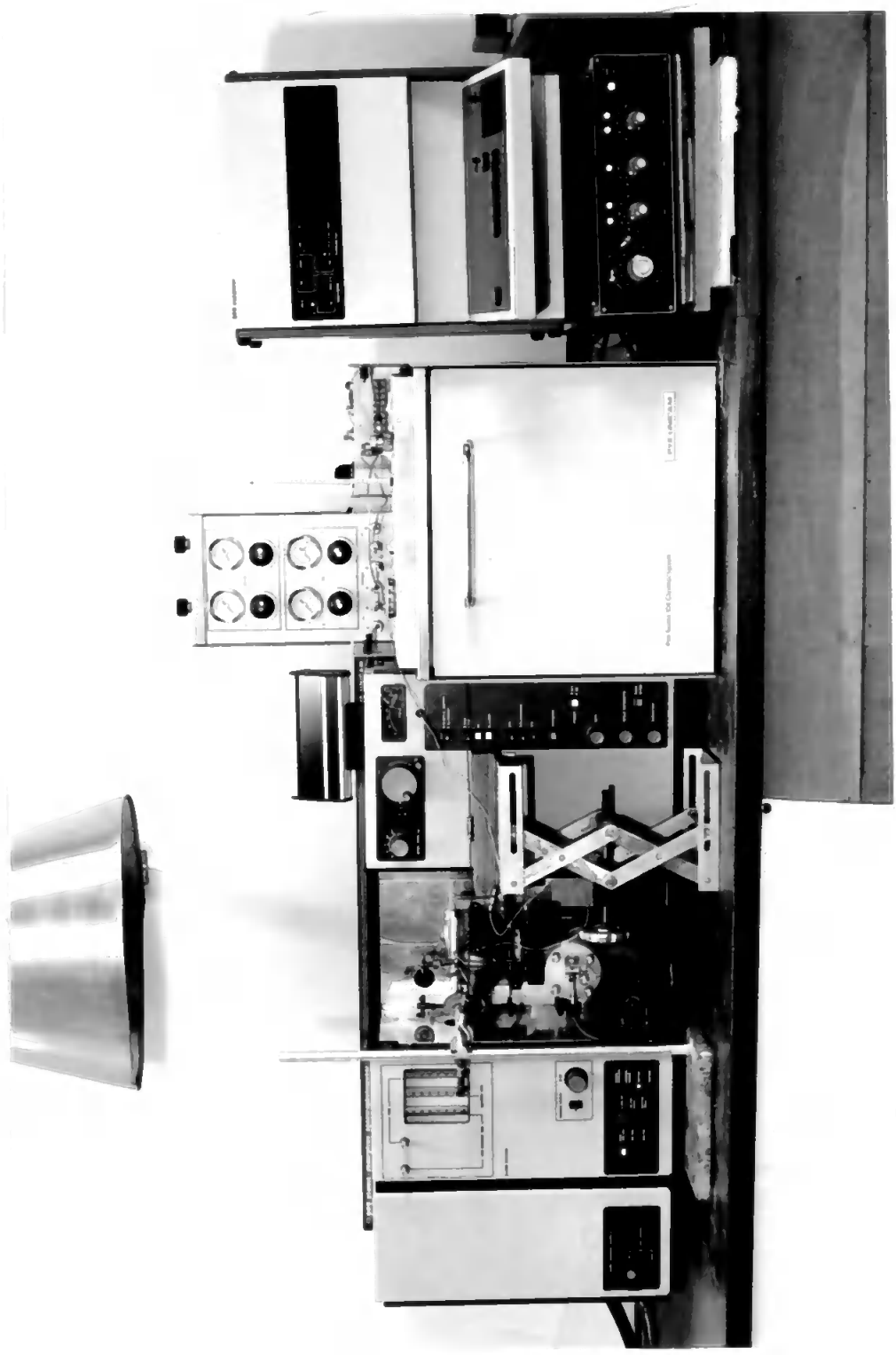
Knife Edge Support for Ceramic Tube

Plate 2

Cradle Support for Ceramic Tube

Plate 3

Experimental Arrangement of Chromatograph and Spectrometer



6 APPLICATIONS OF THE VARIOUS ATOM CELLS DEVELOPED FOR COUPLED GAS CHROMATOGRAPHY ATOMIC ABSORPTION SPECTROSCOPY

6.1 Tetraalkyllead Compounds

Gasoline containing TEL as an antiknock additive was first sold by General Motors Development Co. in Dayton, Ohio, in February, 1923, and the giant Ethyl Gasoline Corporation was formed to exploit the commercial potential. TML was not introduced as a commercial antiknock agent until 1960, and mixed methyl-ethyllead compounds were also used shortly afterwards. Many other organolead compounds exhibit antiknock properties, however, none have proven as commercially viable as the methyl- and ethyl-derivatives. A full discussion of the synthesis, properties and toxicology of commercial organolead compounds may be found elsewhere (282, 283), as can a discussion of the nature of the "antiknock effect" (282). The toxicity of tetraalkyllead compounds was recognised early in their commercial life (283), indeed production of TEL and its addition to gasoline was halted in 1925 for more than a year until the occupational risk had been investigated and hygienic measures for protecting workers had been instituted. The environmental impact of tetraalkyllead from gasoline/petrol is once again the subject of much dispute in the popular press; however, perhaps this should be placed in perspective with lead pollution from other sources, e.g. from water and food.

The fate of organolead compounds in the various environmental reservoirs has been subject to much study. The lead added as tetraalkyllead to fuel enters the environment predominantly in inorganic particulate form in the vehicle exhaust fumes. Turner (284) proposed the use of exhaust filters as an alternative to the reduction of the amount of

antiknock agents added to petrol. It might be argued that this report is not truly independent, coming from an employee of the largest U.K. producer of antiknock agents. Harrison and co-workers (285, 286) have studied the occurence and fate of tetraalkyllead compounds in the atmosphere. They found elevated levels near petrol stations, as have other workers (see Chapter 2, Table 4), and demonstrated rapid decomposition of the tetraalkyllead compound during daylight hours. The toxicological and environmental concern alluded to above demonstrates the need for a simple, specific method of analysis for tetraalkyllead compounds in both gasoline and the environment.

6.1.1 Determination of Tetraalkyllead Compounds in Petrol

The advantage of using metal specific detection for trace metal speciation studies can be demonstrated by comparing the chromatograms obtained using dual ECD/FID and FAAS, atom cell I. The operating conditions for the GC-ECD/FID are given in Table 16, those for the GC-FAAS were the simplex optimum conditions, Table 12, column 1. The resulting chromatograms for a solution of petrol (10%) in iso-octane containing both TML and TEL, using both dual ECD/FID and FAAS detection are shown in figures 16 and 17 respectively, the latter illustrates five consecutive injections of the petrol. Figure 16 shows that whilst it is possible to quantify TML and TEL in petrol using electron capture detection, it would be difficult using flame ionization detection. The universality of response of the latter detector requires all the components of the petrol to be separated. This was not achieved under the conditions used, e.g. Figure 16 shows that the TML peak is masked by the flame ionization response to the iso-octane solvent. The ECD, whilst giving

Figure 16 Gas Chromatographic Separation of a 10% Petrol Solution Using Dual Electron Capture/Flame Ionization Detection

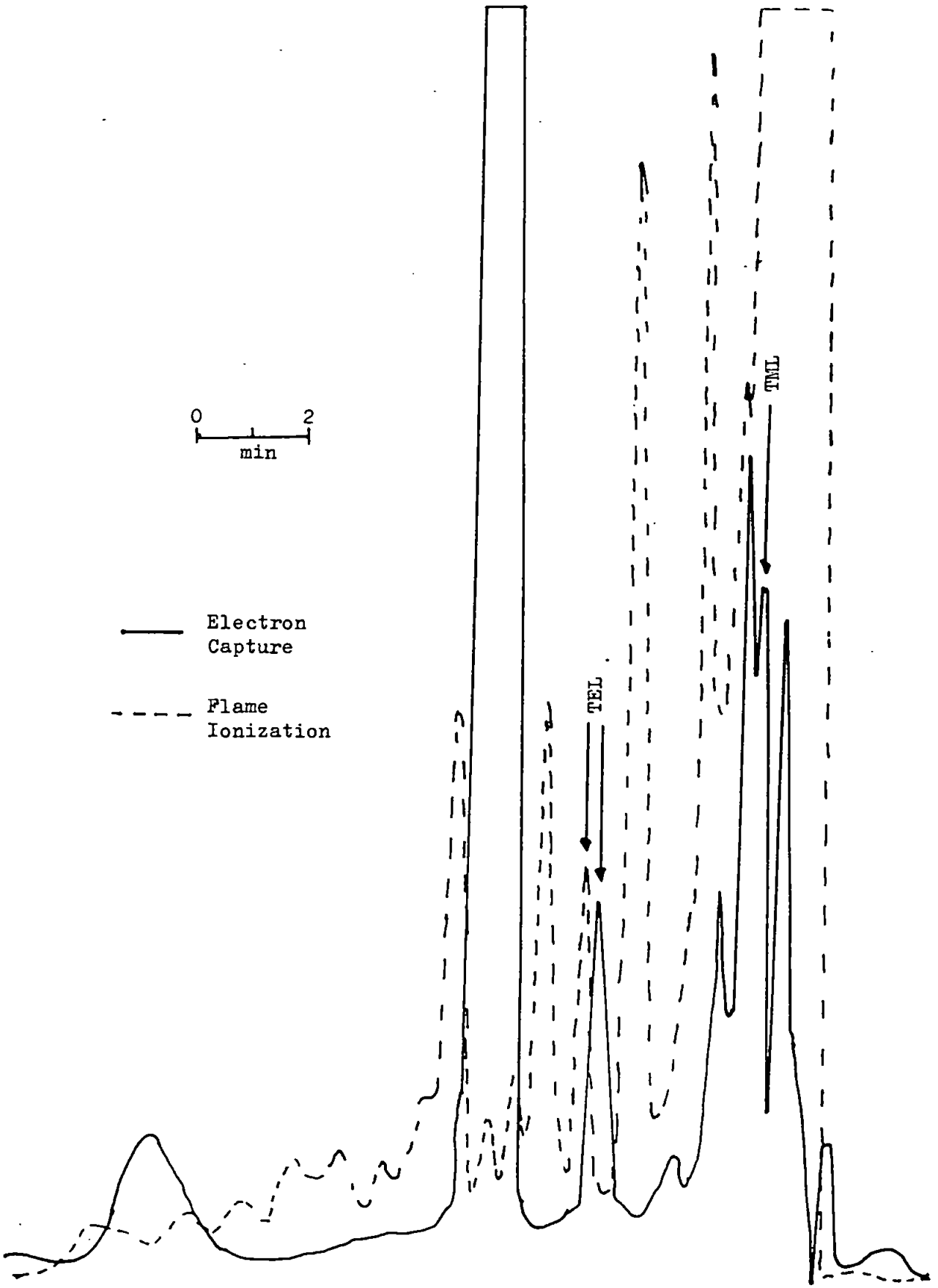


Figure 17 Gas Chromatographic Separation of a 10% Petrol Solution Using Flame Atomic Absorption Spectroscopic Detection with Atom Cell I.

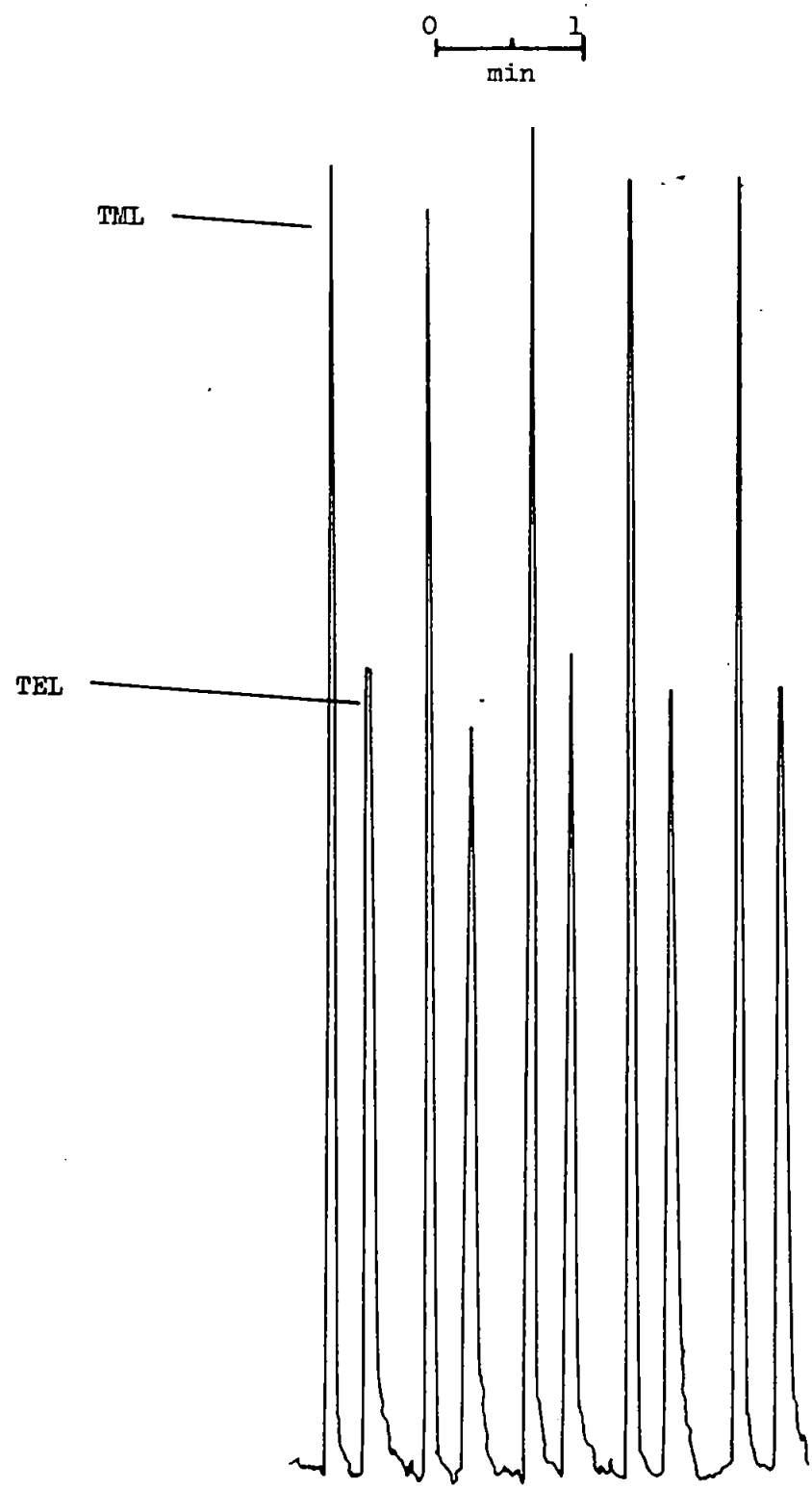


Table 16

Chromatographic Conditions for Analysis of Petrol using Dual Electron Capture/Flame Ionization Detection

Column	7' x 4 mm glass column 10% Carbowax 20M on Chromosorb 750, 80/100 mesh.
Carrier Gas	Nitrogen 30 ml min^{-1} 1:1 split
FID	Air/Hydrogen flow-rates as recommended by manufacturer. Attenuation range of 128 x 10
ECD	Detector Current of 12 x 10^{-9} A Attentuation range of 32

a slightly elevated response to the tetraalkyllead compounds compared with simple saturated hydrocarbons, is extremely responsive to halogen containing species. Thus the ECD responds to the halogen containing scavenger species in the petrol and thus chromatographic resolution is required between these and the tetraalkyllead compounds to avoid any interference. The choice of a polar stationary phase, Carbowax 20M, was unhelpful in achieving sufficient resolution of the matrix peaks for detection using flame ionization or electron capture. On such a polar stationary phase the separation of mainly non-polar solutes is difficult since the amount of time they spend dissolved in the phase is small. Better resolution would have been achieved using a less polar stationary phase; however, using metal specific detection, i.e. FAAS, which does not respond to the non-lead containing organic compounds in the petrol matrix makes such resolution unwanted. The advantage of using a polar stationary phase with the GC-FAAS coupling is that it allows much faster analysis times, i.e. under 1 min. This is much quicker than for the GC-ECD/FID analysis where the analysis time was around fifteen minutes, and even then, complete resolution of all species in the matrix was not achieved.

The coupled GC-FAAS system using atom cell I was used for the determination of TML and TEL in five petrol samples, the results of which are given in Table 17(a).

Table 17(a)

Determination of Lead in Petrol using Coupled Gas Chromatography - Flame Atomic Absorption Spectrometry with Atom Cell I

Petrol No.	Lead concentration (mg/l)	
	TML	TEL
1	160 ± 4	325 ± 9
2	105 ± 5	220 ± 11
3	55 ± 3	115 ± 6
4	235 ± 9	223 ± 9
5	395 ± 8	40 ± 2

Table 17(b)

Total lead in Petrol found by both methods

Petrol No.	Lead concentration (mg/l)	
	GC-FAAS	AAS
1	485 ± 14	490 ± 11
2	325 ± 16	320 ± 7
3	170 ± 9	140 ± 4
4	458 ± 18	460 ± 8
5	435 ± 16	435 ± 8

Total lead figures were obtained for the five petrols using the method of Kashiki et al. (287) in which iodine (3 mg) was added to the petrol (1 ml) before dilution with MIBK and FAAS analysis. It can be seen that (Table 17(b)) good agreement as to the total lead content of the five petrols was found using the two methods, although the precision is better for the total lead analysis, as would be expected.

In British petrols only TML and TEL are added as antiknock agents; however, some continental petrols contain the mixed methyl-ethyl-tetra-alkyllead derivatives. Thus to demonstrate that the coupled system could speciate these compounds, a solution containing the five mixed alkyls was analysed. The separation was optimised using the chromatographic response function as criterion of merit, see Chapter 5, section 5.2.2. The centroid optimum conditions are given in Table 18.

Table 18

Centroid Optimum Conditions for the Separation of Five Mixed Tetraalkyl-lead Compounds using Atom Cell IV

Carrier Gas Flow-Rate/ml min^{-1}	45
Air Flow-Rate/l min^{-1}	4.0
Acetylene Flow-Rate/l min^{-1}	0.6
Hydrogen Flow-Rate/ml min^{-1}	43
Chromatographic Temperature/^{o}C	74
Heating Rate/^{o}C min^{-1}	49
Ceramic Tube-Air/Acetylene Burner Separation/mm	11.0
Ceramic Tube-Hydrogen Diffusion Burner Separation/mm	0

Figure 18 illustrates a chromatogram of a solution of the five mixed lead alkyls (20μg ml^{-1} Pb) in the ratio of 3:4:6:4:4 of Pb. The retention times of the five tetraalkyllead species are given in Table 19. Thus it is evident that good resolution is achieved and that the five lead alkyls may be determined in under two minutes.

Two further applications concerning tetraalkyllead compounds in the environmental and forensic field are alluded to in Chapter 8.

Table 19

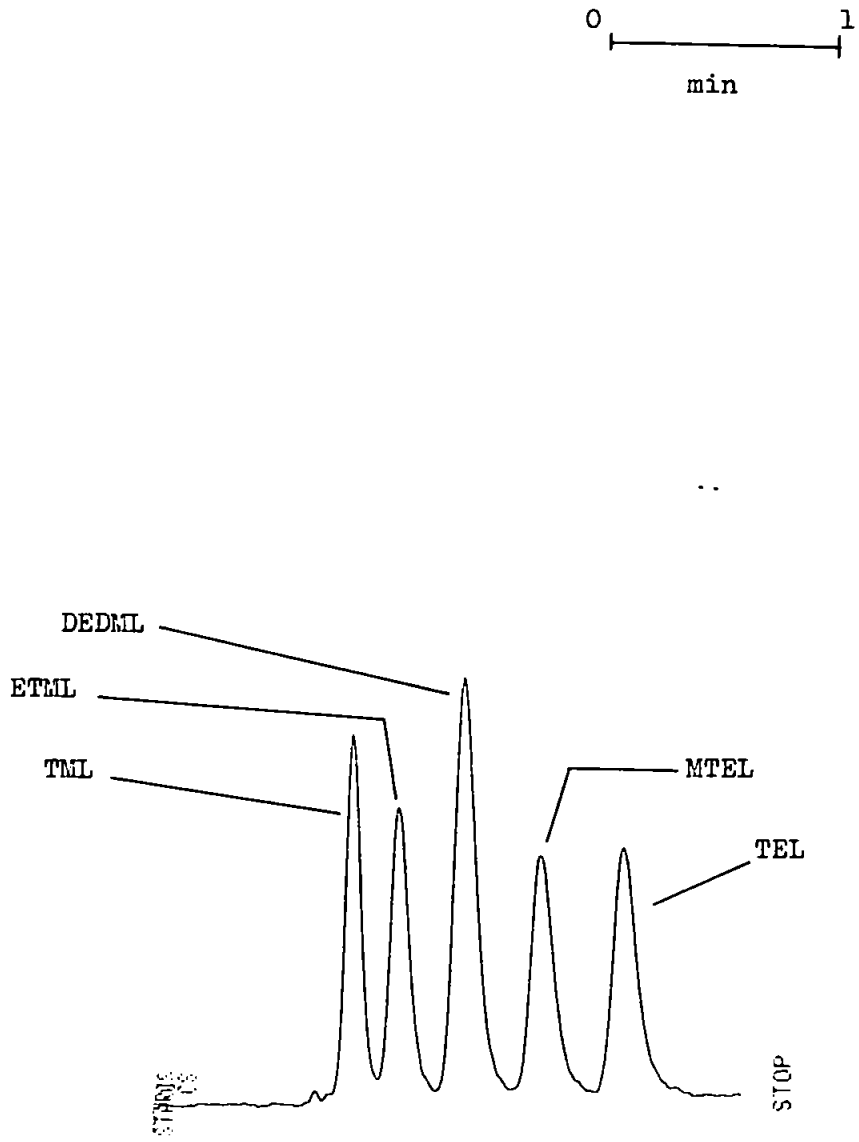
Retention Time Data for the Separation of the Five Mixed Tetraalkyllead Compounds

Species	Retention Time/min
Tetramethyllead (TML)	0.79
Ethyltrimethyllead (ETML)	0.99
Diethyldimethyllead (DEDML)	1.28
Methyltriethyllead (MTEL)	1.62
Tetraethyllead (TEL)	1.99

Figure 18

Coupled Gas Chromatography - Flame Atomic Absorption Spectroscopy

Chromatogram of the Five Tetraalkyllead Compounds using Atom Cell V



6.2 Organomercury Compounds

Around 10^4 tons of mercury are vented into the atmosphere each year by fossil fuel consumption, sulphide ore smelting, cement manufacture and the heating of other materials containing mercury (12). Although the mercuric ion is itself very toxic (2, 12), methylated forms of mercury are much more toxic, see section 1.1.1, and may be concentrated from water or through the food chain by virtue of their high lipid-solubility. Bio-methylation of inorganic mercury, see section 1.1.2, and its resultant cycling between the various environmental reservoirs is well known and most speciation methods have been aimed at differentiating between the various organic and inorganic forms of mercury.

It is known that of the various organo-mercurial compounds, dimethyl- diethyl- and di-n-propyl- mercury are causative of Minamata disease(7). The speciation of these three compounds was used to test the suitability of the atom cells developed for organomercurial determinations. The likely levels of organomercurials in samples of interest will be very low, thus only atom cell IV was considered as this had proved the most sensitive for the speciation of tetraalkyllead compounds.

6.2.1 Experimental

Stock solutions (100 mg l^{-1}) of the dialkylmercury compounds were made weekly by dilution from the pure liquid (Lancaster Synthesis, Leonardgate, Lancaster), by dilution with benzene, all other dilutions were made daily.

Atom cell IV was used in conjunction with the SP 192 (Pye Unicam Ltd., York St., Cambridge) spectrometer, the mercury resonance line at 253.6 nm being monitored with a band pass of 0.8 nm. The chromatographic column used was the same as for the tetraalkyllead work. The operating conditions of the system are given in Table 20, column 2.

6.2.2 Safety

In view of the very toxic nature of these mercury compounds, fairly stringent safety precautions were observed. Manipulation of these compounds and their solutions was performed in a dry box placed in a well vented fume cupboard. Protective gloves were worn and mouth-pipetting avoided.

Disposal of solutions of the organomercurials was preceded by breakdown of the organic mercury compounds to an inorganic form. This breakdown was achieved by reacting the organomercury compounds with a bromate-bromide solution (288).

6.2.3 Speciation of Dialkylmercury Compounds

The coupled GC-FAAS system incorporating atom cell IV was optimised using the variable step size simplex method, see section 5.1. The continuously variable parameters optimised were: air flow-rate, acetylene flow-rate, nitrogen carrier gas flow-rate, hydrogen flow-rate, initial chromatographic temperature, time held at initial temperature, and rate of increase of chromatographic temperature during temperature programme. The range of factor space considered and the centroid optimum values found by the simplex procedure are given in Table 20,

Table 20

Simplex Variables for the Speciation of Dialkylmercury Compounds

Variable	Range	Centroid Optimum Value
Hydrogen Flow-Rate/ml min^{-1}	0-120	25
Nitrogen Flow-Rate/ml min^{-1}	5-120	20
Air Flow-Rate/l min^{-1}	2-5	3.1
Acetylene Flow-Rate/l min^{-1}	0.2-1.0	0.35
Initial Chromatographic Temperature/^{o}C	60-160	92
Hold Time/min	0-5	0
Chromatographic Heating Rate/^{o}C min^{-1}	0-40	25

column 1. Confirmation that the simplex procedure had found the optimum conditions was achieved by carrying out a series of univariate searches. The success of the optimisation can be seen in fig. 19, which illustrates some chromatograms obtained during the univariate search for nitrogen carrier gas flow-rate. Figure 19(b) shows the separation obtained at the centroid optimum flow rate and Figures 19(a) and (c) illustrate separations obtained at flow-rates either side of the optimum. Table 21 gives the detection limits and retention times obtained for the three dialkylmercury species under the optimum conditions found.

Table 21

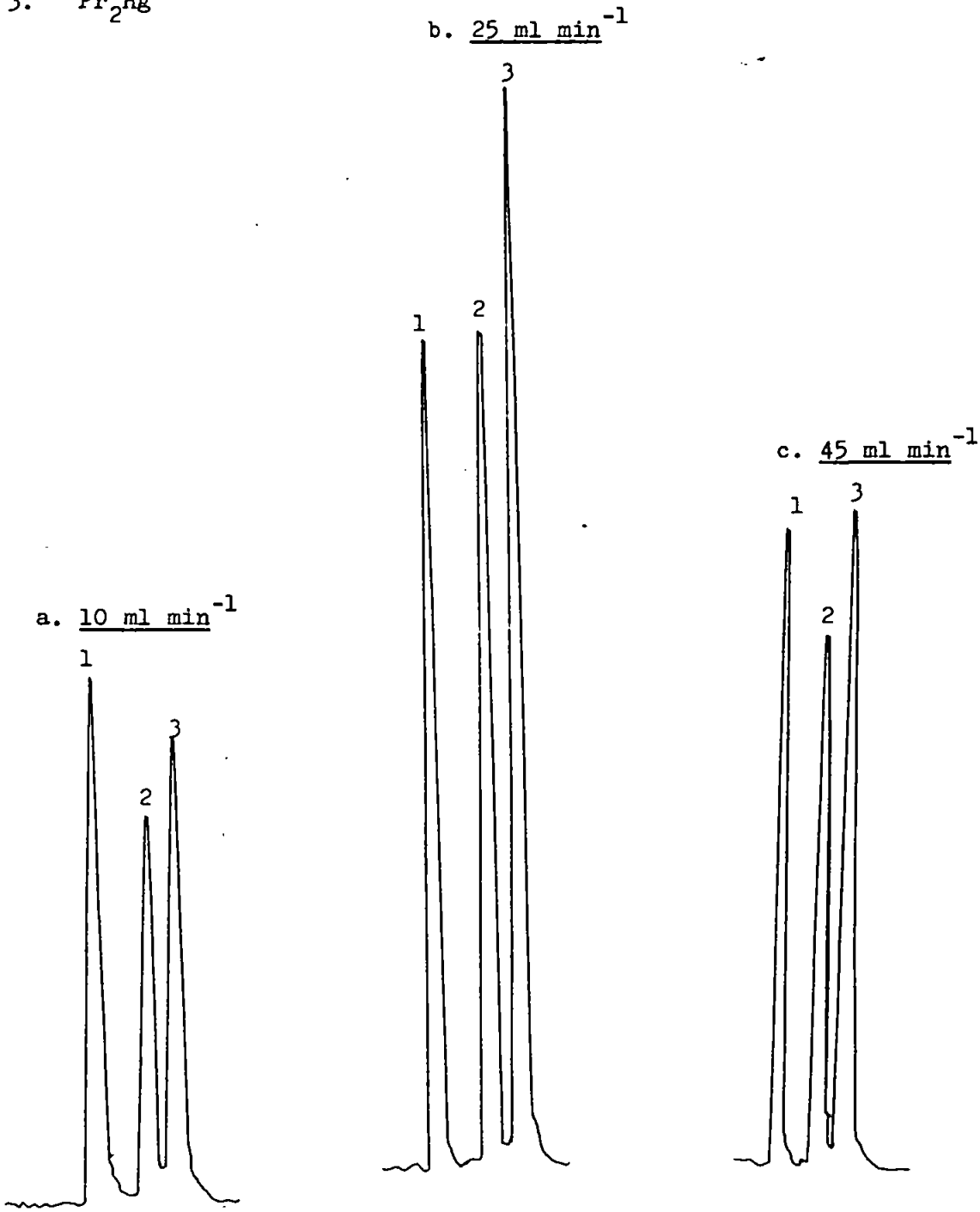
Detection Limits and Retention Times Obtained for the Dialkylmercury Compounds

Species	Detection Limit/pg	Retention Time/min
Me_2Hg	80	1.22
Et_2Hg	120	2.02
$^nPr_2Hg$	95	2.45

Thus coupled GC-FAAS using atom cell IV enables rapid, trace level speciation of organomercurial compounds to be performed.

Figure 19 Chromatograms Obtained During Univariate Search for Nitrogen, Carrier Gas Flow-Rate

1. Me_2Hg
2. Et_2Hg
3. $^nPr_2Hg$



6.3 Organoselenium Compounds

Selenium is well known as an element which is toxic to man, however it is also a trace element which participates in oxidation-reduction reaction, especially in erythrocytes; indeed, it is thought that a body mechanism controls the concentration and oxidation state of selenium (289). The formation of volatile derivatives have been used to enable speciation of the various oxidation states of selenium using gas chromatographic separations. For example, 1,2-diamino-3,5-dibromobenzene can react only with selenium(IV). This reagent has been utilized in conjunction with GC-ECD for the determination of relative amounts of the various oxidation states of selenium in natural waters (290) and human blood (289).

Biomethylation of inorganic selenium compounds is also known to occur; for example, Astralagus racemosus is known to transpire inorganic selenium as organoselenium compounds, notably dimethylselenium and dimethyldiselenium (190, 191).

The applicability of the coupled GC-FAAS system, atom cell IV, to the speciation of volatile organoselenium compounds was evaluated by attempting to speciate dimethylselenium and dimethyldiselenium.

6.3.1 Experimental

Stock solutions (100 mg l^{-1}) of the alkyl-selenium compounds were prepared weekly from pure solutions (Lancaster Synthesis, St. Leonard's Gate, Lancaster) by dilution with n-pentane. Similar precautions to those used with the alkylmercury compound were used when handling these compounds.

Atom cell IV was used in conjunction with the SP 9 (Pye Unicam Ltd., York St., Cambridge) spectrometer. The selenium resonance line at 196 nm was monitored using a 1.0 nm bandpass and background correction. Despite the low wavelength of the selenium line sufficient energy throughput was achieved using a selenium hollow cathode lamp. The chromatographic column used was 3% Dexsil on Chromosorb 750 and the operating conditions used are given in Tables 22 and 23.

6.3.2 Speciation of Alkylselenium Compounds

Sufficient experience had been gained with the coupled GC-FAAS system that satisfactory conditions for the speciation of the organoselenium compounds could be identified without resort to the simplex method. These conditions are given in Table 22.

At the selenium resonance line (196 nm) a response was found to the solvent entering into the atom cell, i.e. a solvent peak. That a response from the solvent was achieved intimates that the background absorption was above two absorbance units, since the SP 9 is capable of correcting for this background level. The presence of a solvent peak was not seen when the lead or mercury lines, at 283.3 and 253.6 nm lines were monitored.

From a first approximation of Rayleigh's law of light scattering the scattered intensity is:

$$T = 24 \pi^3 N \nu^2 / \lambda^4 \qquad \ldots 6(1)$$

For particles having a diameter less than one-tenth of the wavelength of the incident radiation the scattered intensity, T, is directly

Table 22

Chromatographic Conditions for the Speciation of Organoselenium Compounds

Glass Column	1.5 m x 4 mm i.d. 3% Dexsil 300 on Chromosorb 750
Initial Temperature	100°C
Heating Rate	20°C min^{-1}
Injector Temperature	150°C
Interface Temperature	120°C
Nitrogen Carrier Flow Rate	60 ml min^{-1}
Hydrogen Flow Rate	150 ml min^{-1}

Table 23

Spectrometer Conditions for the Speciation of Organoselenium Compounds

Wavelength/nm	196
Lamp Current/mA	6.0
Bandpass/nm	1.0
Air/l min^{-1}	5.0
Acetylene/l min^{-1}	1.0
Ceramic Tube - Air/Acetylene burner separation/mm	10.0
Ceramic Tube - Hydrogen Diffusion burner separation/mm	0.0

proportional to the total number of particles, N, and the square of the particle volume. It is also inversely proportional to the fourth power of the wavelength, λ. Thus scattering of small particles shows a strong wavelength dependence. For example, assuming N and ν to be the same, on moving from the lead line (283.3 nm) to the selenium line (196 nm), the scattered intensity would be 4.4 times greater. Additionally, molecular fragments formed by incomplete combustion might be expected to absorb more strongly at low wavelengths, i.e. higher energy.

The response of the solvent peak could be reduced by increasing the hydrogen flow-rate to the diffusion burner, Fig. 20. At high hydrogen flows, 540 ml min^{-1}, the size of the solvent response is negligible due to more efficient combustion of the solvent; however, the response to selenium is also reduced. This is probably due to the high gas flow purging the ceramic tube more rapidly than at lower flow-rates. Thus the atomic species spend less time in the observation zone resulting in a decreased selenium response. This effect can be seen (Figure 21) by comparison of the chromatograms of the selenium compounds at hydrogen flow-rates of 150 and 540 ml min^{-1}. At the higher flow-rate the solvent peak is very small but comparison of the chromatograms shows a decreased selenium response at higher hydrogen flows. Thus it was found better to work routinely at the 150 ml min^{-1} and use the temperature programme to resolve the solvent and dimethylselenium peaks. The detection limits and retention times, Table 24, demonstrate that rapid and sensitive detection of the alkylselenium compounds is possible with a linear working range from 1 to 50 ng.

Figure 20

The Effect of Hydrogen Flow-Rate on Peak Height Response

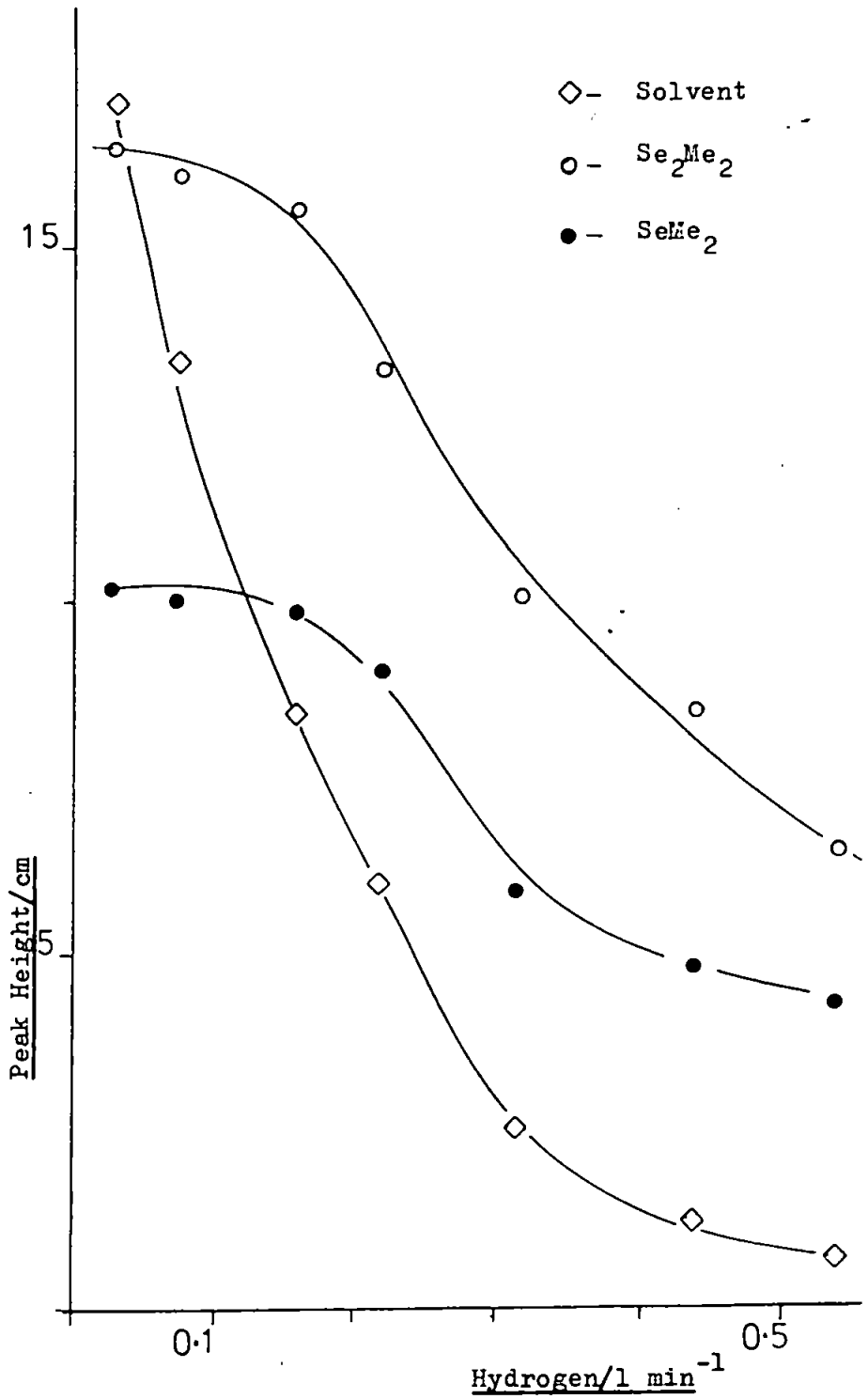
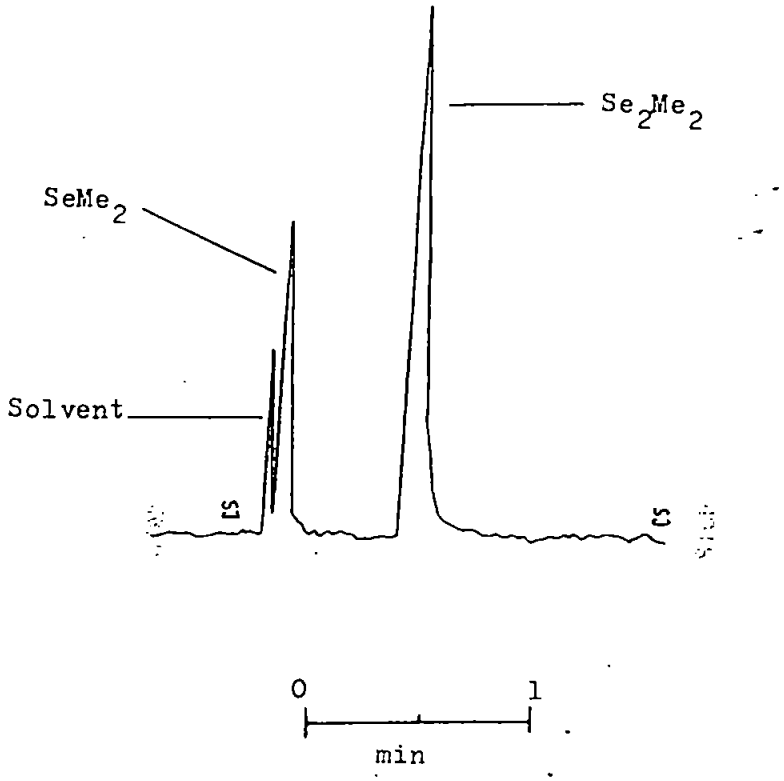


Figure 21 Coupled Gas Chromatography - Flame Atomic Absorption Spectroscopy Chromatograms

A. Hydrogen Flow = 150 ml min^{-1}



B. Hydrogen Flow = 540 ml min^{-1}

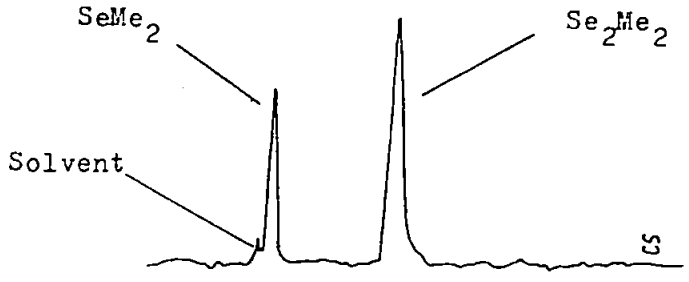


Table 24

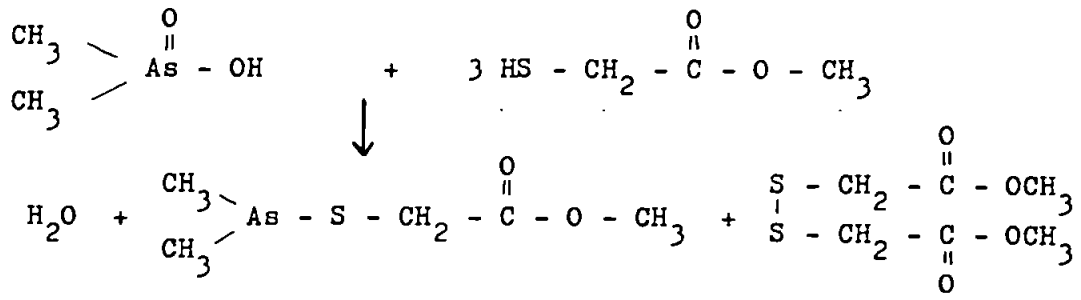
Detection Limits and Retention Times Obtained for the Organoselenium Compounds

Species	Detection Limit/ng	Retention Time/min
Me_2Se	0.12	0.36
Me_2Se_2	0.13	0.93

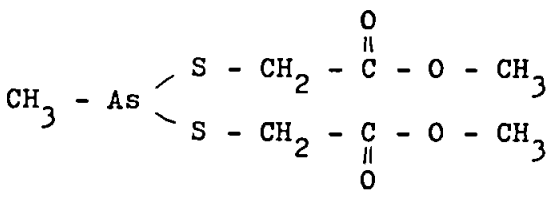
6.4 Organoarsenic Compounds

Interest in the speciation of arsenic compounds is stimulated by two main areas. Firstly, the use of arsenic compounds as pesticides and herbicides both as inorganic arsenic salts and as organoarsenicals such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). As with many other metals the toxicity, biological activity and environmental fate depends on the molecular form of occurrence. Secondly, it has been shown that different arsenic compounds interconvert in the environment (291) by both chemical and biological pathways (17, 292, 293); for example, Sanders and Windam (294) showed arsenate to be assimilated by marine phytoplankton and to be finally released into solution after reduction and methylation. As the methylated forms of arsenic are apparently much less toxic than their inorganic parent compounds, speciation of arsenic compounds yields more useful information than total arsenic levels. It is interesting to note that whilst the biomethylation of inorganic arsenic constitutes an efficient mode of detoxification for many other metal compounds, for example mercury, the reverse is the case.

To enable speciation of arsenate, arsenite, MMA and DMA by GC, volatile derivatives must be prepared prior to separation. The preparation of hydrides prior to GC separation is fraught with problems including molecular rearrangements (92). These problems have led to many attempts to produce suitably volatile and thermally stable derivatives to enable gas chromatographic separation (295-297), all of which had drawbacks. Recently, Beckermann (298) demonstrated using GC-FID and GC-MS that MMA and DMA formed stable volatile derivatives with methylthioglycolate (MTG). The reaction for DMA is:



Thus reduction from As(V) to As(III) occurs with the formation of a disulphide prior to the third mole of thiol reacting to give the thioarsinite compound. The derivative formed with MMA has the structure:



Beckermann (298) suggested that inorganic arsenic should also form a MTG derivative, presumably $As(MTG)_3$, but did not report the isolation or separation. Thus by using the derivatization procedure of Beckermann (298) and using the coupled GC-FAAS system developed, metal specific speciation of these compounds was attempted.

6.4.1 Experimental

Atom cell IV in conjunction with the SP 9 spectrometer and Pye 104 series gas chromatograph was used. The operating conditions are given in Tables 25 and 26. The column chosen was recommended by Beckermann (298) as it gave good peak symmetry.

Standard (10^3 mg l^{-1}) solutions of MMA, DMA and arsenite were prepared and to aliquots (10 ml) buffer solution (2 ml, 0.91 M disodium hydrogen phosphate/0.3 M citric acid/5% w/v EDTA) was added and the pH

Table 25

Chromatographic Conditions for the Speciation of Arsenic Methylthioglycolate Derivatives

Column	1.5 m x 4 mm i.d. Glass, 2.5% Silicone XE-60 on Chromosorb G AW-DMCS
Column Temperature/^{o}C	245
Injector Temperature/^{o}C	245
Interface Temperature/^{o}C	300
Nitrogen Flow-Rate/ml min^{-1}	60

Table 26

Spectrometer Conditions for the Speciation of Arsenic Methylthioglycolate Derivatives

Wavelength/nm	193.7
Lamp Current/mA	6.0
Bandpass/nm	1.0
Mode	Background Correction
Air Flow-Rate/l min^{-1}	5.0
Acetylene Flow-Rate/l min^{-1}	1.1
Hydrogen Flow-Rate/ml min^{-1}	300
Ceramic Tube - Air/Acetylene burner separation/mm	11.0
Ceramic Tube - Hydrogen diffusion burner separation/mm	0.0

adjusted with concentrated nitric acid to between pH 3 - 5. Methylthioglycolate (0.5 ml) and cyclohexane (10 ml) were added and the mixture shaken for five minutes vigorously. The organic layer then contained the thioarsenite derivative and working standards were made by dilution with cyclohexane.

6.4.2 Speciation of the Arsenic-Methylthioglycolate Derivatives

Analysis of the aqueous layers by ICP-OES and FAAS indicated that the percentage efficiency of derivatization was 100, 80 and 75 for DMA, MMA and arsenite respectively. Preliminary work using GC-FID was consistent with the finding of Beckermann (298) that the elution order was cyclohexane, dimethylthioarsenite derivative, disulphide, monomethylthioarsenite derivative. No flame ionization response was obtained for the arsenite derivative. The reasons for this lack of response could be:

a. failure to prepare the derivative;

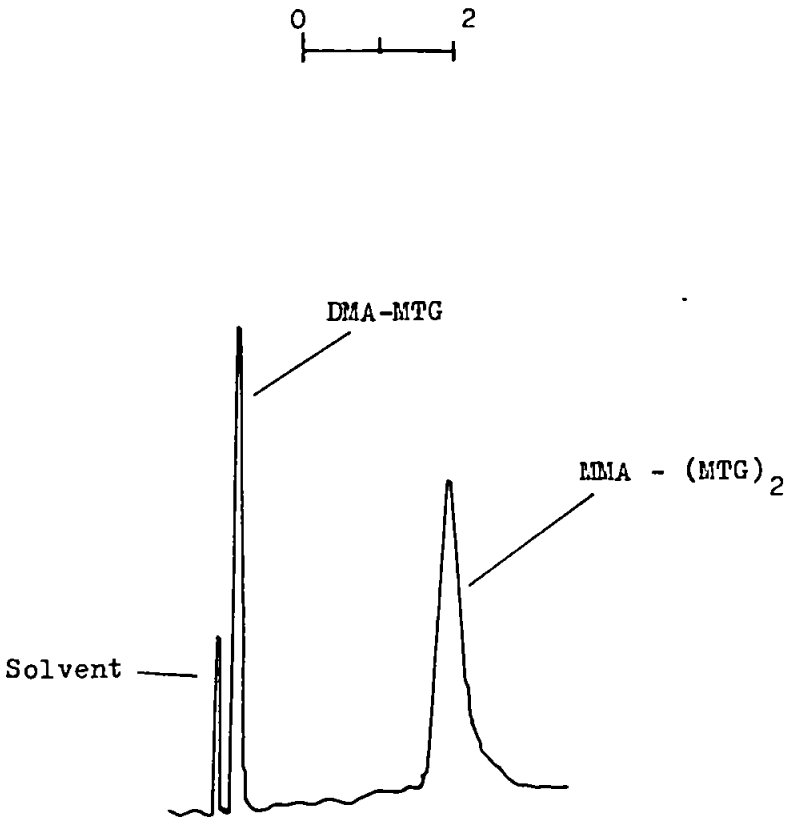
b. insufficient volatility for GC analysis;

or c. poor thermal stability resulting in breakdown of the derivative on the column.

The fact that 75% of the arsenite appeared to be in the organic phase intimated that preparation of a derivative had been at least partly successful. From the chromatographic behaviour of the MMA and DMA derivatives it seems unlikely that the arsenite derivative would suffer from poor thermal stability. Thus the most probable cause for this lack of response would appear to be insufficient volatility for gas chromatographic analysis under the conditions used for the other derivatives.

Figure 22

Coupled Gas Chromatography - Flame Atomic Absorption Spectroscopy Chromatogram of the Thioarsenite Derivatives Obtained using Atom Cell IV



Even operating the column at its maximum permitted temperature, 275°C, failed to yield a response for the arsenite derivatives. Thus to enable inorganic arsenic to be determined by this procedure, different liquid phases must be investigated; however, it was thought that such an investigation was outside the scope of this thesis, and that the speciation of the MMA and DMA derivatives would be sufficient to demonstrate the applicability of the coupled GC-FAAS system developed to the speciation of volatile arsenic compounds.

The separation achieved using the coupled GC-FAAS system is illustrated in Fig. 22, for a 1.0 µl injection of a solution containing the dimethyl- derivative (50 mg l^{-1}) and the monomethyl- derivative (200 mg l^{-1}) in cyclohexane. The detection limits and retention times are given in Table 27. The detector response was linear up to 350 ng of arsenic. The levels of detectability achieved were not really sufficiently low to follow arsenic transformations in environmental samples; however, the facility for a concentration step to be introduced in the extraction of the derivatives exists. The concentration step could quite reasonably be expected to lower the concentration

Table 27

Detection Limits and Retention Times Obtained for the Thioarsenite Derivatives

Species	Detection Limit/ng	Retention Time/min
DMA - MTG	0.8	0.45
MMA - $(MTG)_2$	1.7	3.26

detection limit by a factor of ten which would then make the GC-FAAS applicable to environmental monitoring.

6.5 Conclusion

The various applications of the atom cells developed demonstrate one of the primary advantages of metal selective detection, namely the ease by which unequivocal chromatographic interpretation may be made. As a result of the selective response to metals faster analysis times are possible since normally only the species containing the metal of interest require resolution. At low wavelength where light scatter problems from the combustion of the solvent are exacerbated, the metal containing species must also be resolved from the solvent. This only increases the number of species to be resolved by one and does not reduce analysis times significantly.

The short retention times resulting from metal selective detection reflects the reduced time a species spends dissolved in the stationary phase. The shorter this time is, then the smaller the peak width will be. A commensurate increase in peak height is thus achieved aiding the achievement of low levels of detection. Cursory comparison of the detection limits obtained for the different metallic species compared to those for lead show poorer detection limits, especially for the organoarsenic compounds. If, however, a comparison of the solution detection limits for lead, 0.01 ppm, and arsenic, 0.1 ppm (150), are made and a compensation for the peak width of the organometallic species made, then from the TML detection limit of 17 pg Pb a predicted detection limit of 0.68 ng As for the dimethylthioarsenite derivative is obtained. This compares closely to the detection limit of 0.8 ng As obtained

experimentally for this species.

The linear ranges obtained for the various metals illustrate the short linear range, an inherent limitation of any absorption technique. The similarity of design of the flame atom cells enables this problem to be alleviated somewhat, for example, by simply removing the ceramic tube from above the flame a linear working range for lead of 0.1 to 300 ng may be spanned.

Thus the atom cells developed for coupled GC-FAAS have been shown to be capable of rapid, metal specific detection at low levels for a variety of metal species. This coupled with the simplicity and robustness and ready demountability of the atom cells, indicates that the GC-FAAS systems developed can provide the necessary analytical tools to enable trace metal speciation studies of volatile species to be undertaken from a sound analytical base. The arsenic speciation work illustrates the weakness of GC in that it is limited to the separation of volatile species. The speciation of the four reducible forms of arsenic, namely DMA, MMA, As(V) and As(III) could be more easily achieved using a liquid chromatographic separation. One such separation will be outlined in Chapter 7.

7 DEVELOPMENT OF ATOM CELLS FOR TRACE METAL SPECIATION BY COUPLED LIQUID CHROMATOGRAPHY - ATOMIC SPECTROSCOPY USING HYDRIDE GENERATION

7.1 INTRODUCTION

The need for arsenic speciation has been discussed, see Chapters 1 and 6. It would be particularly useful to speciate the two common inorganic oxidation states, along with DMA and MMA. Interest in the speciation of two other compounds, namely arsenobetaine and arsenocholine, is also increasing (231, 263). Liquid chromatography is finding increasing favour for the separation of these compounds. The levels of interest, being trace, preclude a direct flame coupling, i.e. simply feeding the HPLC eluent to the uptake capillary of the flame and the most popular coupling has been LC-AAS using graphite furnace atomization (218, 231-233, 237, 239). Although graphite furnace atomization offers excellent limits of detection for a single atomization the time required to make an injection into a furnace necessitates that very low chromatographic flow-rates are used. This not only increases analysis times, but also has the effect of spreading each arsenic species over a large time span which makes the detection limit for the whole chromatographic peak much larger than that of a single atomization. For example, Woolson and co-workers (218) found a linear range for As of 0.1-2 ng for single atomizations, but the linear range for the chromatographic peak was 5-200 ng.

The use of hydride generation after separation by liquid chromatography offers a continuous monitor for reducible arsenic species. Ricci et al. (237) used ion chromatography in conjunction with hydride generation into an electrothermally heated quartz tube for atomic absorption

detection. They obtained detection limits of 10 ppb As using 0.8 ml injections into the ion chromatograph. The separation of reducible arsenic species required either a gradient elution necessitating column restabilization for one hour between determinations, or two separate isochratic separations. With the isochratic approach, the column required re-equilibration for one hour after every 10-15 samples. Thus, although more than satisfactory sensitivity had been achieved, the analysis time was no improvement on existing LC-GFAAS systems, indeed the repeated column equilibration makes the method of Ricci (237) less desirable for routine work. This chapter will demonstrate that rapid analysis can be coupled with sensitive detection for As using HPLC coupled with hydride generation FAAS/FAFS and ICP-OES.

7.2 HYDRIDE GENERATION

Arsenic resonance lines lie in the far ultraviolet spectral region where flame absorption can produce unfavourable signal-to-noise ratios. A conventional air/acetylene flame absorbs 62% of the incident radiation at 193.7 nm, whereas the argon-hydrogen diffusion flame absorbs only about 15% (299). This hydrogen diffusion flame is cooler than the air/acetylene flame, and interferences due to molecular absorption and incomplete salt dissociation are common. Thus by forming the volatile arsenic hydride matrix separation is possible thus minimising interferences in the flame. The major advantage of hydride generation is, however, in the increased efficiency in sample transport. The use of hydrides in atomic absorption spectroscopy has been extensively reviewed by Godden and Thomerson (300).

The basic requirement for the generation of arsines is a supply of hydride ions, and these may be provided by using various reduction cells. The work of Schmidt and Royer (301) proved to be a benchmark in hydride generation by proposing the use of sodium tetrahydroborate (III) as reductant. Initial problems with reagent purity (302) were overcome by manufacturers and the use of sodium tetrahydroborate in pellet form became popular, as it was economical and convenient. The use of single pellets is ideal for discrete injection techniques (303), whilst for continuous flow systems the use of tetrahydroborate (III) solutions is preferable (304). Problems of instability with tetrahydroborate solutions can be obviated by making the solution 0.1 molar in sodium hydroxide (305).

The atomization of covalent hydrides has been achieved satisfactorally in flames, argon/hydrogen diffusion flame (304), and tubes either electrically (306) or flame heated (302). Earlier work in our laboratory (304) has shown that by careful design of flame used for atomization detection limits comparable to those using more complex systems could be achieved.

7.3 EXPERIMENTAL

7.3.1 Instrumentation

Spectrometer:

SP 9 (Pye Unicam Ltd.) equipped with background correction facility.

Eluent Delivery System:

6000 A (Waters Associates Ltd., Massachusetts) equipped with a Waters U6K injection valve.

Computing Integrator:

3390A Reporting integrator (Hewlett Packard, Pennsylvania).

Peristaltic pumps:

Schuco Mark III Minipumps (Schuco Scientific, London).

7.3.2 Reagents

Stock solutions (1000 mg l^{-1}) of arsenate, arsenite, MMA and DMA were prepared weekly from the solids, all other dilutions prepared daily, by dilution with deionized doubled distilled water. Sodium borohydride solutions were prepared from the solid (98% Aldrich Chemical Co.) by dilution with sodium hydroxide (0.1 molar). All other solvents and acids were of Analar quality unless stated otherwise.

7.4 PRELIMINARY DEVELOPMENT

Previous work in this laboratory (304) had developed a continuous flow hydride generation system, using two peristaltic pumps. This was used to determine total arsenic and selenium. The pumps delivered: sample in hydrochloric acid (5 molar), 7.0 ml min^{-1}, sodium tetrahydroborate solution, 2.5 ml min^{-1}, which passed through a 28 turn mixing coil (2.5 mm. i.d.), and then into a standard gas-liquid separator arrangement. The arsine was purged from the gas-liquid separator up into a small hydrogen diffusion flame by an argon purge gas, 120 ml min^{-1}. The diffusion flame was burnt on an inverted "Y" glass burner, 0.6 mm.i.d., with a fuel gas flow of 180 ml min^{-1}, and situated in the light path of the spectrometer. This basic hydride generation/atomization system was then adapted for coupling to LC.

The main drawback of any post column technique for HPLC is large dead volumes which can cause band spreading, thus decreasing the peak height response and hence reducing detectability. Thus in an effort to develop a post column arrangement which gave minimal band spreading, an injection system was used, Fig. 23. Injections of arsenic solutions were made through a septum injector into the solution mixing branch (2.5 mm. i.d.). The mixture passed through a mixing coil (2.5 mm. i.d.) into the gas-liquid separator to be purged up into the flame. Since only 1.0 µl injections of arsenic solutions were made, it was reasonable to assume that band spreading from the injection procedure would be negligible and hence any band broadening would arise from the hydride generator. The hydrochloric acid and sodium tetrahydroborate solutions were pumped at 1.5 ml min^{-1} by the peristaltic pumps. The hydride generation was accompanied by evolution of hydrogen, 72 ml min^{-1}, from reaction of excess tetrahydroborate (III) solution with the acid. This flow of hydrogen segmented the flow of solution up to the gas liquid separator and helped to minimise band spreading by diffusion. The length of the mixing coil was varied from 0 to 36 turns and the best length, 6 turns, gave maximum peak height with a minimum of band spreading. The point of introduction of the arsenic solution into the acid stream affected the band spreading obtained. The best introduction point was just before the point at which the tetrahydroborate (III) solution was added. In this position minimal band spreading was seen. This hydride system was then coupled to a high performance liquid chromatograph with the eluent being introduced to the reaction manifold just prior to the introduction point of the tetrahydroborate (III) solution. This experimental arrangement is schematically represented in Fig. 24.

Figure 23 Schematic Diagram of Hydride Generation System used in Preliminary Work

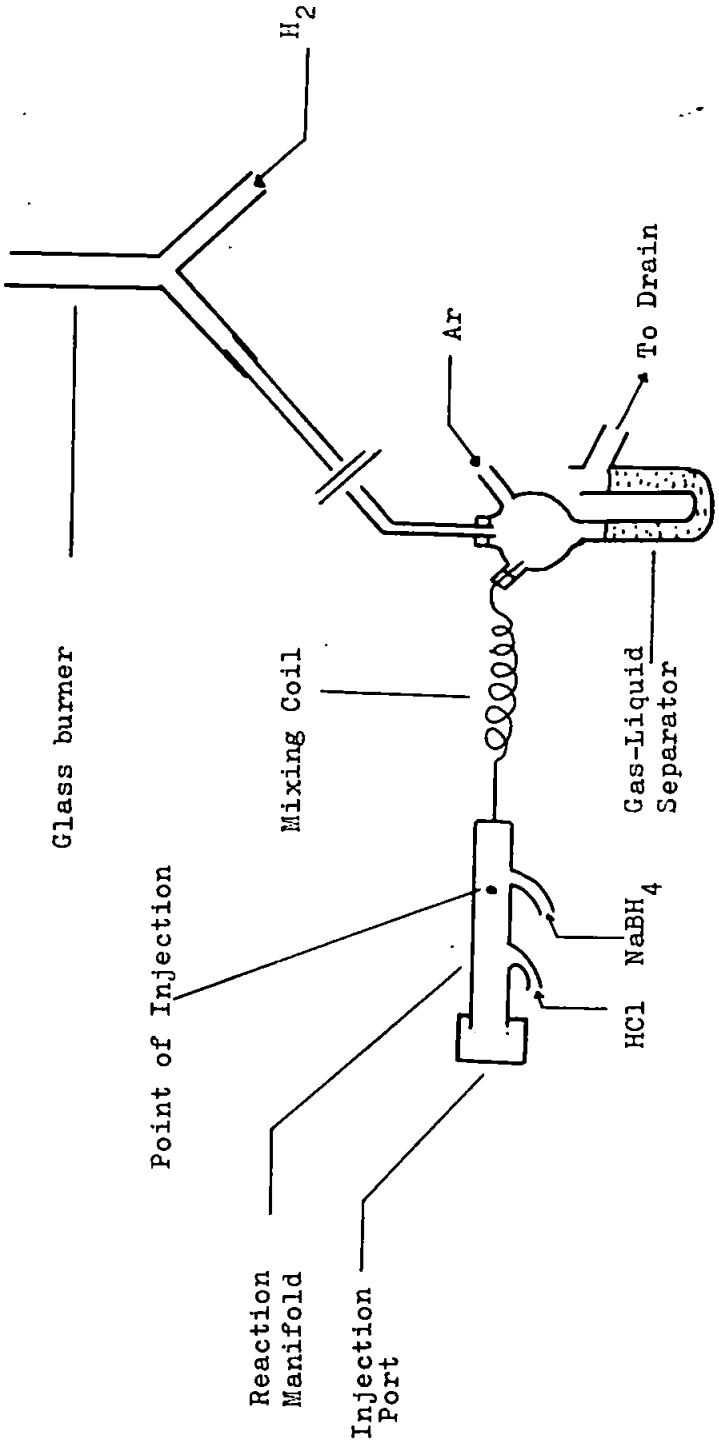
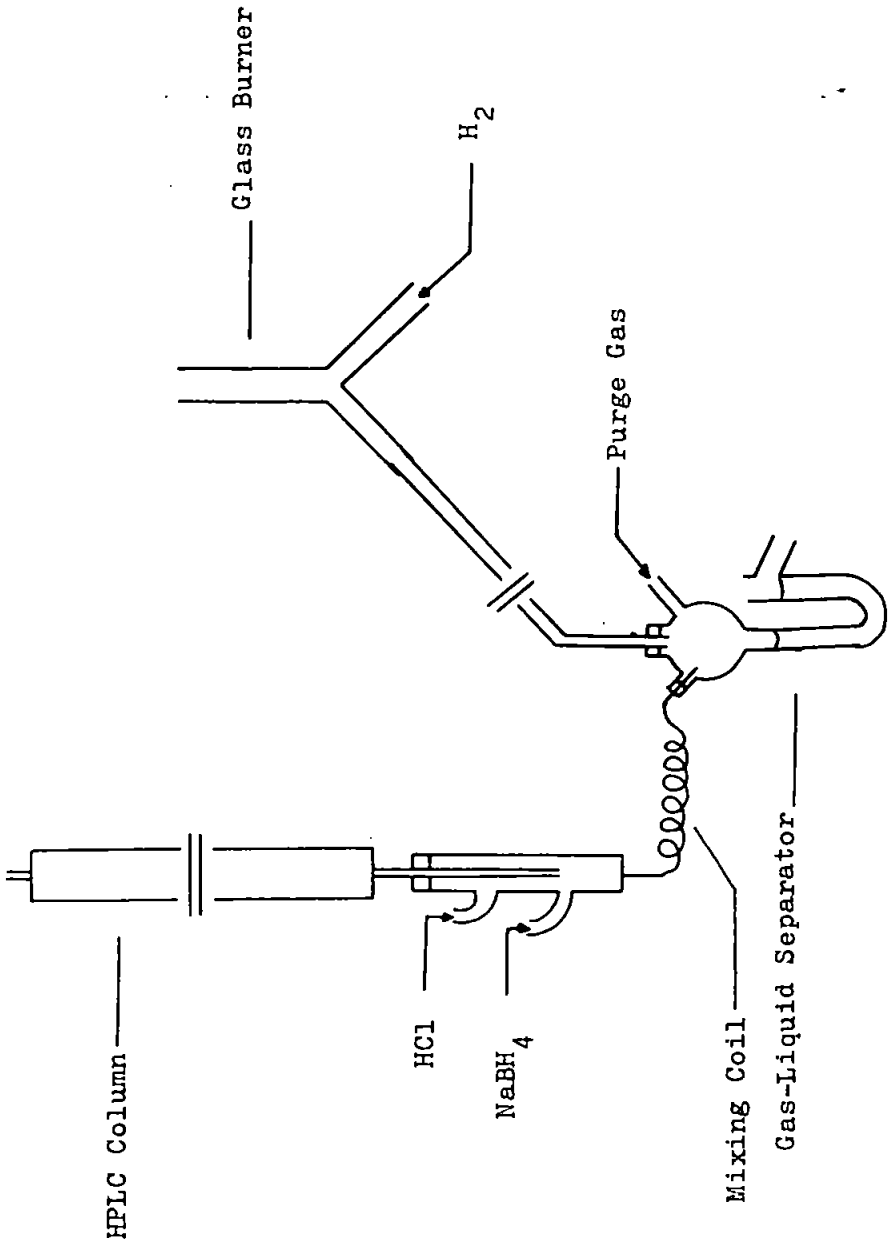


Figure 24

Schematic Diagram of HPLC-Hydride-FAAS/FAFS Coupling



7.5 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY - HYDRIDE GENERATION - FLAME ATOMIC ABSORPTION SPECTROSCOPY SPECIATION OF ARSENIC COMPOUNDS

7.5.1 Choice of Chromatographic Conditions

The majority of published LC atomic spectroscopic couplings for arsenic speciation, see Chapter 3, used reverse phase columns, only Ricci et al. (237) used ion chromatography and encountered problems in that extensive re-equilibration times were required between determinations. HPLC columns (250 x 5 mm. i.d. and 100 mm. x 5 mm. i.d.) were packed with both 3 μm and 5 μm particle size Hypersil-ODS packing. Initial separations indicated that the 3 μm Hypersil-ODS column (250 x 5 mm. i.d.) column would provide the best resolution and was thus used in further work.

Reverse phase columns retain polar compounds most effectively when the ionization of the species is suppressed, thus for the four arsenic species an acid medium should provide optimum resolution. To this end a modified universal buffer (307) over the pH range 1.8 to 7.54, orthophosphoric acid, 1.37×10^{-2} to 1.37 to 10^{-5} mol dm^{-3}, and sulphuric acid, from 1.8×10^{-3} to 1.8×10^{-6} mol dm^{-3} were considered. No resolution of the arsenic species was obtained with the buffer system and sulphuric acid gave better resolution than when orthophosphoric acid was used as eluent. The sulphuric acid eluent system was then investigated further. The ionic strength of the sulphuric acid eluent was varied between 1.8×10^{-3} and 1.8×10^{-6} mol dm^{-3} for an eluent flow-rate of 0.8 ml min^{-1}. Figures 25(a) and 25(b) illustrate the separations achieved at the extremes of ionic strength variation and Figure

Figure 25 Effect of Ionic Strength of Eluent on Chromatographic Separation

(a) = 1.8×10^{-3} mol dm^{-3}

(b) = 1.8×10^{-6} mol dm^{-3}

(c) = 1.8×10^{-5} mol dm^{-3}

Flow-rate = 0.8 ml min^{-1}

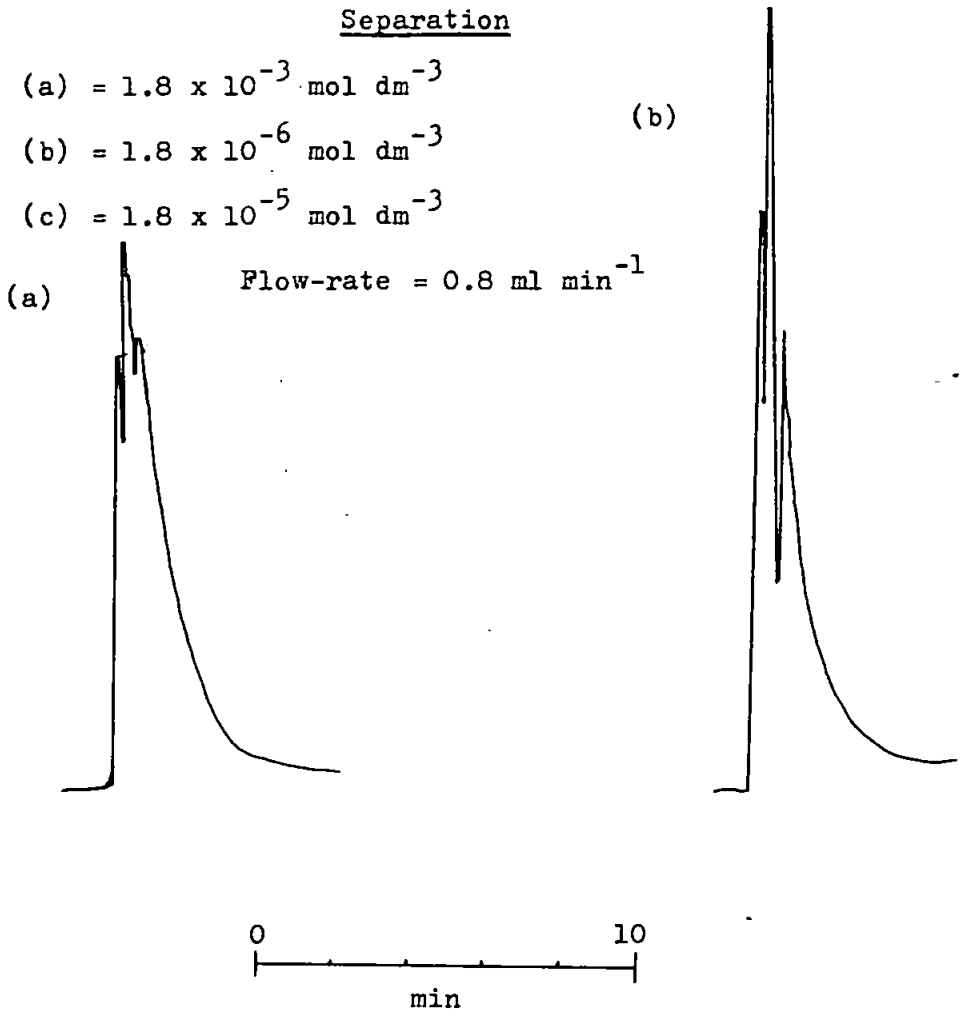
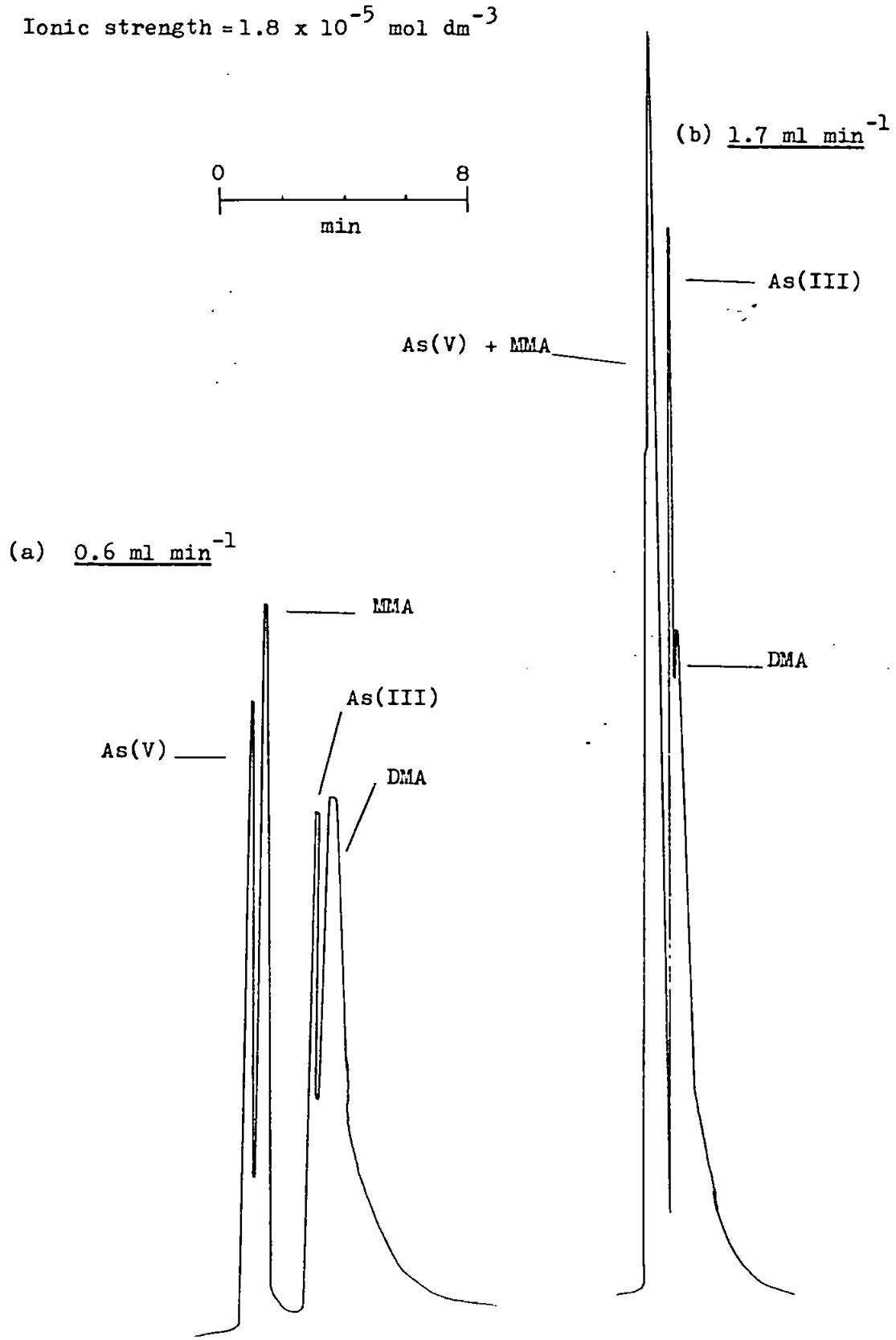


Figure 26 Effect of Eluent Flow-Rate on Chromatographic Separation

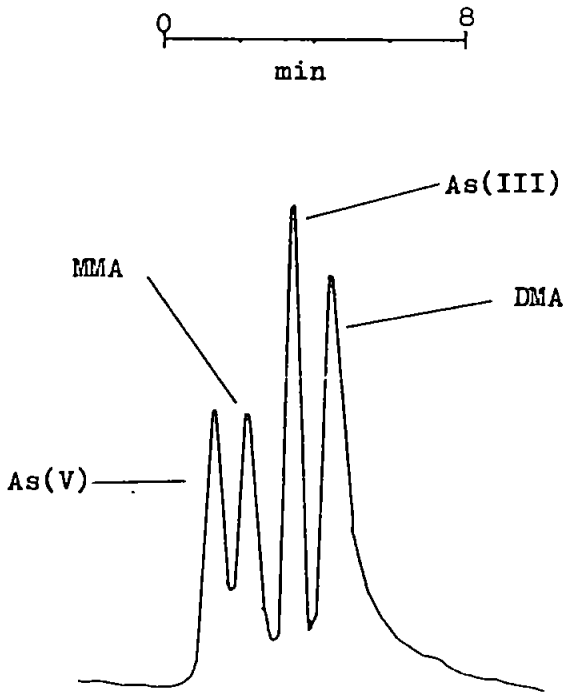


25(c) shows the best separation at this flow rate, the acid ionic strength being 1.8×10^{-5} mol dm^{-3}. In an effort to optimise the separation the eluent flow-rate was varied between 0.6 and 1.7 ml min^{-1}, Fig. 26 illustrates the separations achieved at the two extremes of flow-rate. At the high flow-rate arsenate/MMA are resolved from arsenite/DMA, whereas at the low flow-rate the four species are very nearly completely separated; however the DMA peak is beginning to tail considerably. If the flow-rate were to be reduced further then complete resolution would appear possible, however, this would increase the tailing of the DMA peak and lengthen the analysis time. Thus a flow programme was designed to separate the four arsenic species. Starting the flow programme at 0.5 ml min^{-1} ensured resolution of the four species, then stepping the flow-rate up to 1.5 ml min^{-1} after the elution of MMA minimised the tailing of the DMA peak. This optimal separation is illustrated in figure 27, using 1.8×10^{-5} mol dm^{-3} sulphuric acid at 0.5 ml min^{-1} for 5 min., then 1.5 ml min^{-1} until DMA has eluted. The retention times for the four arsenic species were 3.84, 4.54, 6.24 and 7.29 minutes for arsenate, MMA, arsenite and DMA respectively.

Satisfactory results were obtained using the following column packing procedure. The column was packed with propan-2-ol (100 ml up-flow, 100 ml down-flow at 8000 psi), washed with sulphuric acid eluent (400 ml) and conditioned with ten injections of a solution of the four arsenic species at the 1 mg l^{-1} level. Only sulphuric acid should be used since some other eluents, notably phostate ions, can adversely affect the resolution, although washing with propan-2-ol (100 ml) partially restored the column performance. Washing of the column in propan-2-ol (50 ml) and storage in the same solvent allowed consistent resolution

Figure 27

Optimal Separation Obtained Using Flow Programme



profiles to be obtained over extended periods of time. The chromatographic conditions are summarized in Table 28. Having achieved an adequate separation the hydride generation system was then optimized.

Table 28

Chromatographic Conditions for Arsenic Speciation

Column:	Hypersil-ODS, 3μm, 250 x 5 mm. i.d.
Eluent:	Sulphuric Acid, 1.8×10^{-5} mol dm^{-3}
Flow-Rate:	0.5 ml min^{-1} for 5 min, then 1.5 ml min^{-1}

7.5.2 Optimization of Hydride Generation System

The arsine generation reaction for the four arsenic compounds was dependant on hydrochloric acid concentration, see Fig. 28. Low acid concentration, i.e. between 1 and 2 mol dm^{-3}, favoured hydride formation for the organoarsenical species, whereas high acid concentration, i.e. between 9 and 12 mol dm^{-3}, was optimal for the inorganic arsenic species. Thus an acid concentration of 2 mol dm^{-3} was considered the best compromise for the hydride generation of both inorganic and organic species.

The effect of sodium borohydride concentration, figure 29, was simpler. On increasing the concentration from 0.5% w/v, the detector response to arsenic increased for all the arsenic species until 2% w/v where it plateaued off. Above 2% w/v sodium borohydride concentration no further increase in arsenic response was gained, thus this concentration was used for all further work.

Figure 28 Effect of Acid Concentration on Hydride Formation

50μl Injection of a solution 20 mg l^{-1} in As(V), DMA and MMA and 10 mg l^{-1} in As(III).

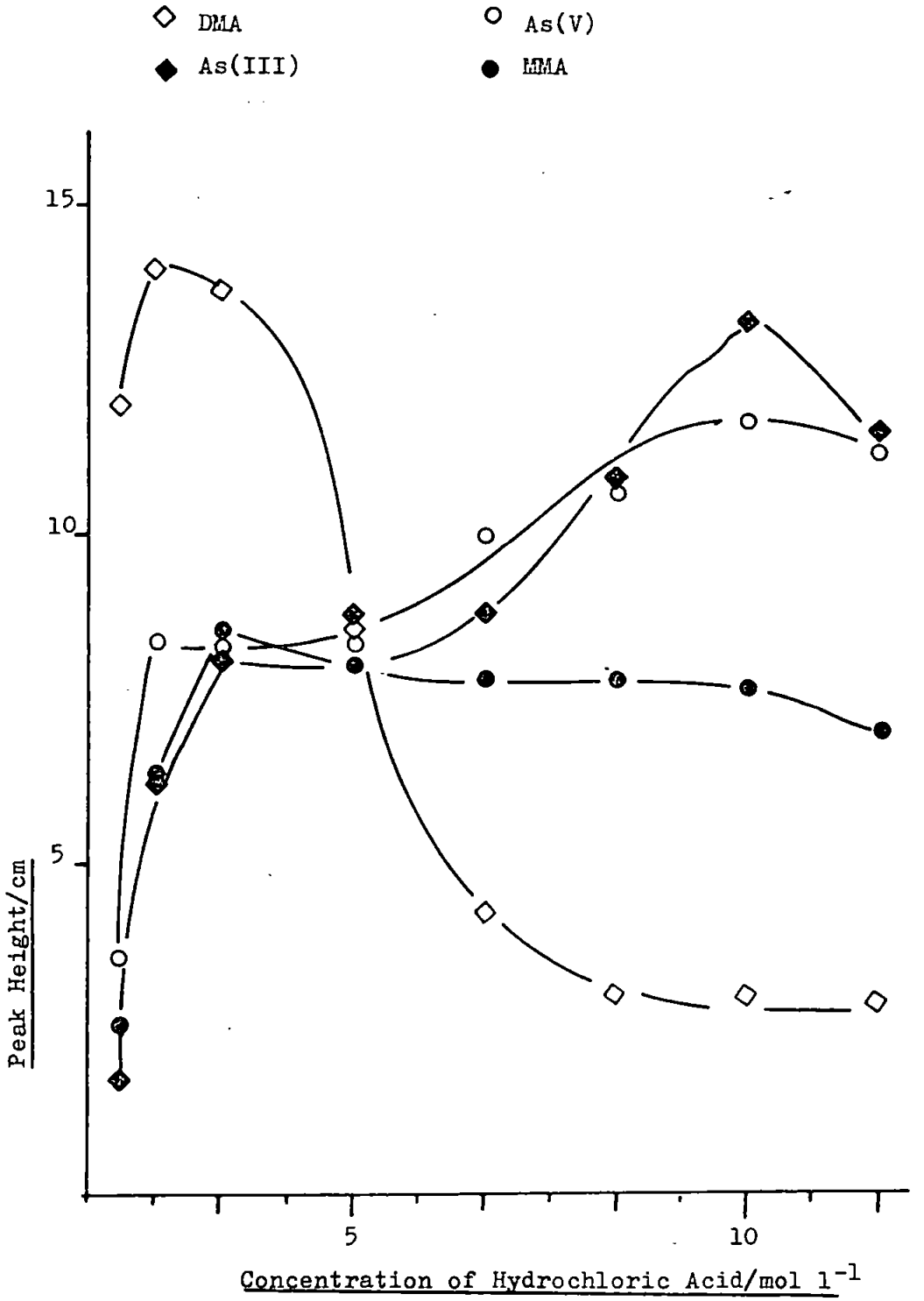
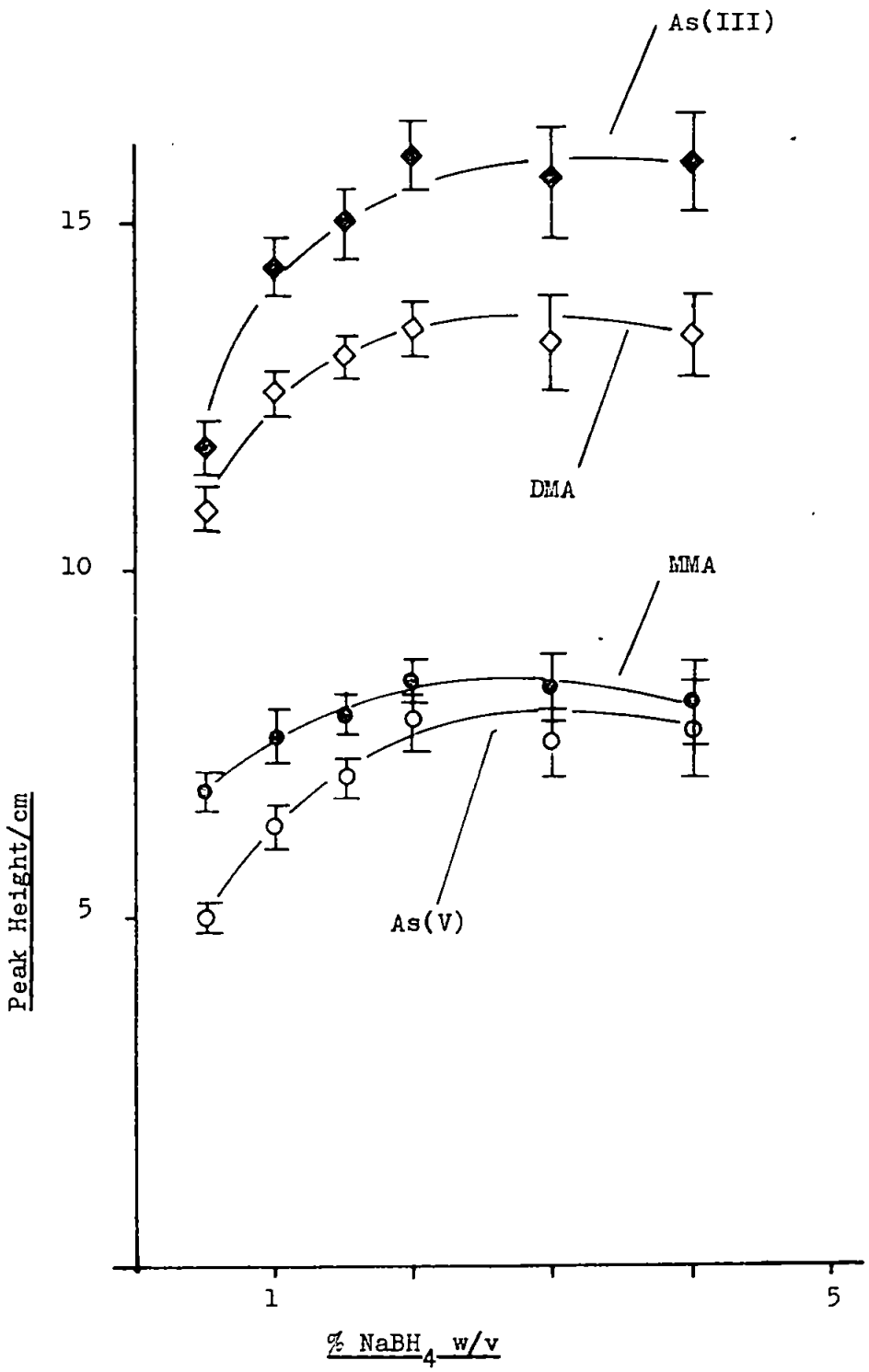


Figure 29 Effect of Sodium Tetrahydroborate (III) Solution Concentration on Hydride Formation



Varying the gas flow, which purged the generated arsines from the gas/liquid separator, figure 30, was found to affect both the response and band spreading of the arsenic species. Below a flow rate of 40 ml min^{-1}, excessive peak broadening resulted in insufficient chromatographic resolution between the four arsenic peaks. At high flow rates, i.e. above 150 ml min^{-1}, the residence time of the arsines in the flame atom cell was reduced, thus leading to a lowered response for arsenic. Accordingly, 100 ml min^{-1} was chosen as the best compromise. The hydride generation conditions are summarised in Table 29.

Table 29

Hydride Generation Conditions for Arsenic Species

Hydrochloric Acid	2 mol dm^{-3}, 1.5 ml min^{-1}
Sodium Tetrahydroborate	2% w/v, 1.5 ml min^{-1}
Purge Gas Flow-Rate	Argon, 100 ml min^{-1}
Fuel Gas Flow-Rate	Hydrogen, 180 ml min^{-1}

The success of the HPLC-hydride FAAS coupling is demonstrated by the separation achieved, Fig. 27, and by the detection limits obtained, Table 30, column 1. The detection limits should be improved by the use of flame atomic fluorescence for arsenic specific detection.

Figure 30

Effect of Purge Gas Flow-Rate on Arsenic Response

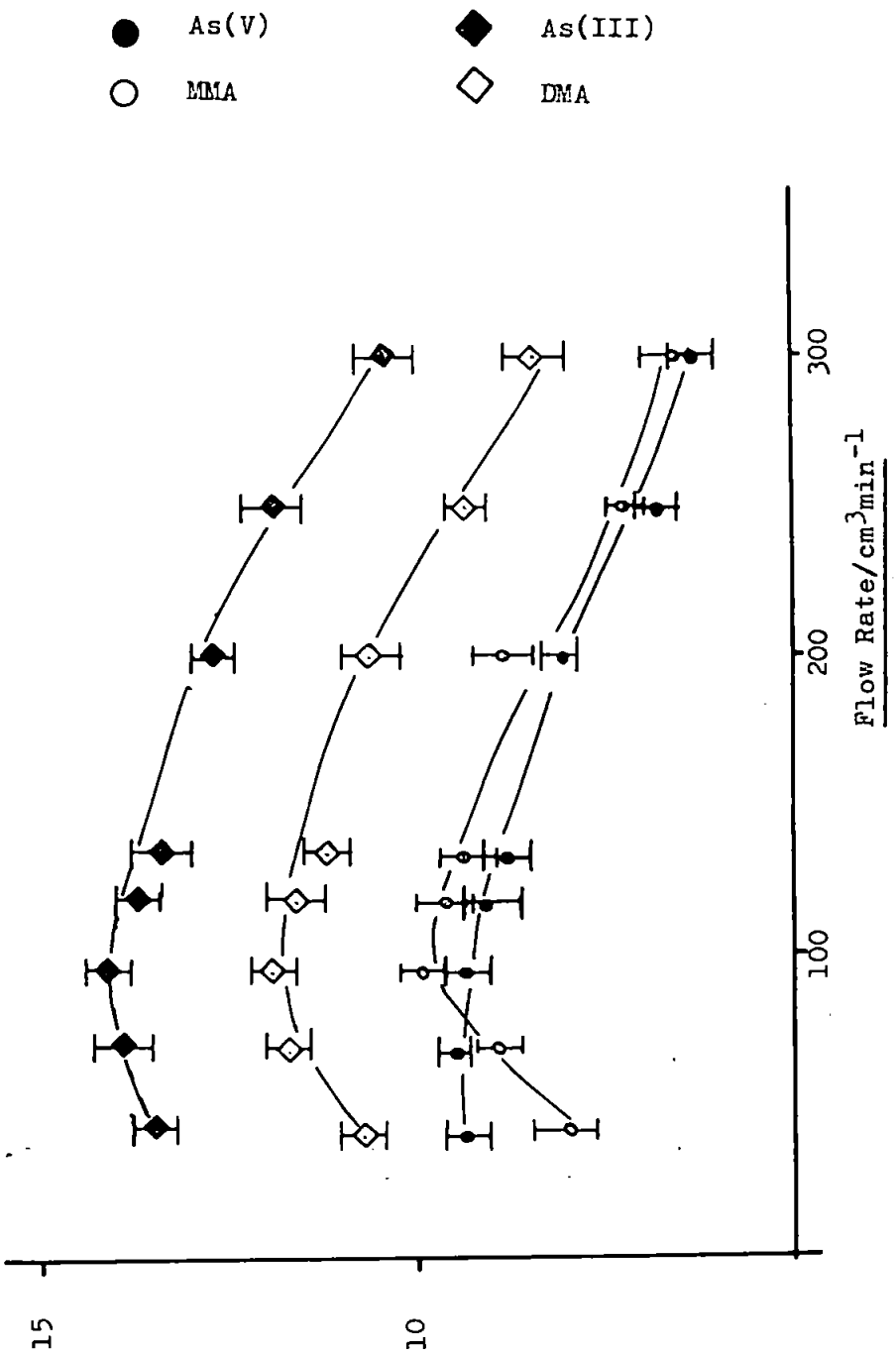


Table 30

Detection Limits Obtained for Arsenic Species

Species	Detection Limit/ppb As		
	FAAS	FAFS	ICP-OES
Arsenate	40	27	128
MMA	43	24	140
Arsenite	10	6	51
DMA	24	18	112

7.6 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY - HYDRIDE GENERATION - FLAME ATOMIC FLUORESCENCE SPECTROSCOPY FOR THE SPECIATION OF ARSENIC COMPOUNDS

The same chromatographic, Table 28, hydride generation, Table 29, and flame conditions were used in conjunction with FAFS as were used with FAAS detection. The radiation source used was an electrodeless discharge lamp, microwave-excited, in a ¾λ Broida cavity at 40W forward power. Detailed description of the equipment may be found elsewhere (304). The best signal-to-noise ratios were obtained using front face 45^{o} illumination, confirming the observation of Ebdon *et al.* (304), the spectrometer being used in the emission mode.

The detection limits using FAFS detection, Table 30, column 2, and linear working ranges were evaluated for the four arsenic species. The detection levels are only a factor of two better than those obtained using FAAS; this was thought to be due to the inability to operate the radiation source in a sufficiently intense manner. Thus, since no significant gain in detectability of arsenic was gained using this source and FAFS, FAAS would appear to be the preferable method of detection for the hydride species given the greater simplicity of operation and better precision.

7.7 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY - HYDRIDE GENERATION - INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY FOR THE SPECIATION OF ARSENIC COMPOUNDS

7.7.1 Introduction

The use of ICP-OES as a detection system offers the possibility of multi-element detection. The geometry of the source gives a freedom from self absorption effects even at quite high concentrations and thus long linear ranges are possible with this source.

Thompson et al. (308, 309) used continuous flow hydride generation into an all-argon ICP for the simultaneous detection of total As, Sb, Bi, Se and Te. In their studies, they found that if the sodium tetrahydroborate (III) concentration increased above 1.5% m/v, at 4.5 ml min^{-1}, the response to the metalloids decreased, and proposed that this was probably due to changes in the plasma caused by the introduction of more hydrogen or by dilution of the hydrides. At such tetrahydroborate concentrations, their plasma became unstable and easily extinguished. Thompson et al. (309) "optimized" the plasma by a series of univariate searches using the signal-to-noise ratio as the criterion of merit. They found that a Fassel-type torch gave best detection limits, but that it could not tolerate hydrogen flows above 150 ml min^{-1} using 2.7 kW forward power. No mention of increased background levels was reported. Fry et al. (310) used cold trapping of the generated arsine not only as a preconcentration step, but also to separate the arsine from the hydrogen prior to introduction into the plasma. They found a background problem if sodium tetrahydroborate (III) pellets were used, caused by CO_2 passing into the plasma. The CO_2 arose as a reaction

by-product from the $MgCO_3$ used as a pelletizing agent.

Since there was no consensus of opinion as to the best plasma operating conditions to use for the detection of arsines, initial work was carried out using conditions found optimal for working with arsenic solutions in previous work in this laboratory (311).

7.7.2 Experimental

A Radyne R50P 27 M Hz free running r.f. generator with integral gas box (Radyne Ltd., Wokingham, Surrey) was used with a demountable torch (312). The monochromator used was a 0.5 m. Ebert scanning grating monochromator (Model 82-529-5P, Jarrell-Ash) with entrance optics comprising of a 2.5 cm. focal length quartz lens, 1:1 image, slitwidth 25 μm and a slit height of 16 mm. The signal, at the 228.8 nm As(I) line, from the photomultiplier (R 106, Hamamatsu T.V. Co. Ltd., Japan) passed through a linear picoammeter amplifier (L M 10; Chelsea Instruments Ltd., London) and was monitored using a reporting integrator (Model 33090A, Hewlett Packard, Pennsylvania). All quoted power levels refer to power coupled into the plasma as measured calorimetrically (313, 314). The optimum plasma conditions (311) are given in Table 29, column 1.

The HPLC and hydride generation conditions were as before.

7.7.3 Optimisation of Plasma Performance

Initial results from the introduction of arsine into the plasma using the solution optimum conditions, Table 31, column 1, showed that

Table 31

Centroid Optimum Plasma Conditions for Arsenic

	Solution	Hydride
Plasma Gas/l min^{-1}	12.3	9.0
Coolant Gas/l min^{-1}	5.4	6.5
Injector Gas/l min^{-1}	0.4	0.42
Viewing Ht./mm	18	27.5
Power/KW	0.59	0.70

a large increase in background emission occurred, thus causing a reduction in the signal-to-background ratio, SBR. This was thought to result from the simultaneous introduction of hydrogen into the plasma. Under the hydride generation conditions used, Table 29, 72 ml min^{-1} of hydrogen were evolved and swept up into the plasma.

Thus the plasma operating conditions were optimised, using the modified simplex method, see Chapter 5. The SBR, which has been demonstrated to be a viable criterion of merit for plasma optimisation (314), was used to optimise the ICP. The continuously variable parameters optimised were: the height of observation above the load coils, power coupled into the plasma, coolant argon flow-rate, plasma argon flow-rate and argon purge gas flow-rate. This latter flow purged the generated arsines and hydrogen from the gas-liquid separator up the injector tube of the plasma torch and through the plasma fireball.

The optimum conditions indicated by the simplex, Table 31, column 2, were confirmed by a series of univariate searches, Fig. 31(a) to (e),

Figure 31(a)

Univariate Search for Coolant Argon

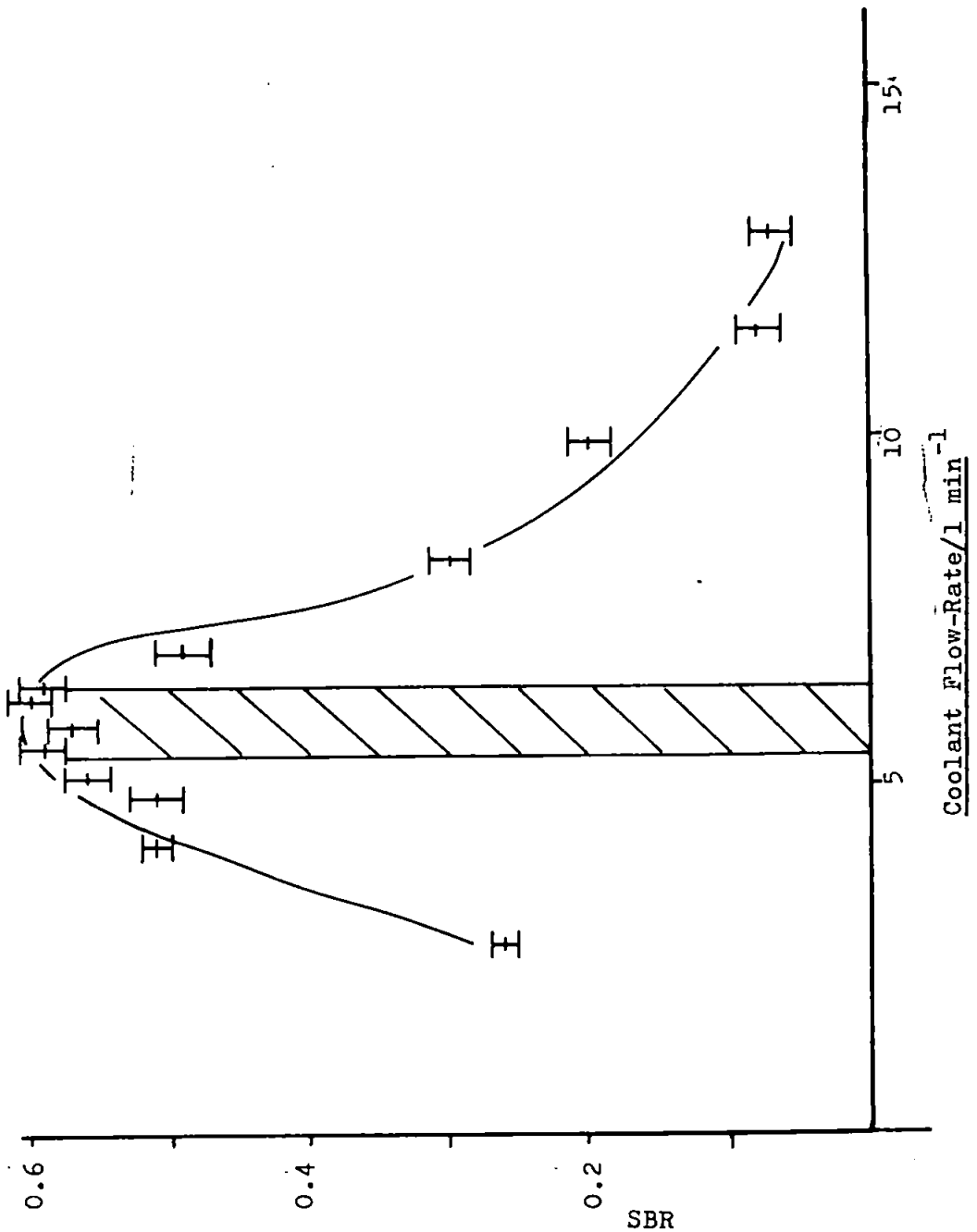


Figure 31(b)

Univariate Search for Argon Plasma Gas

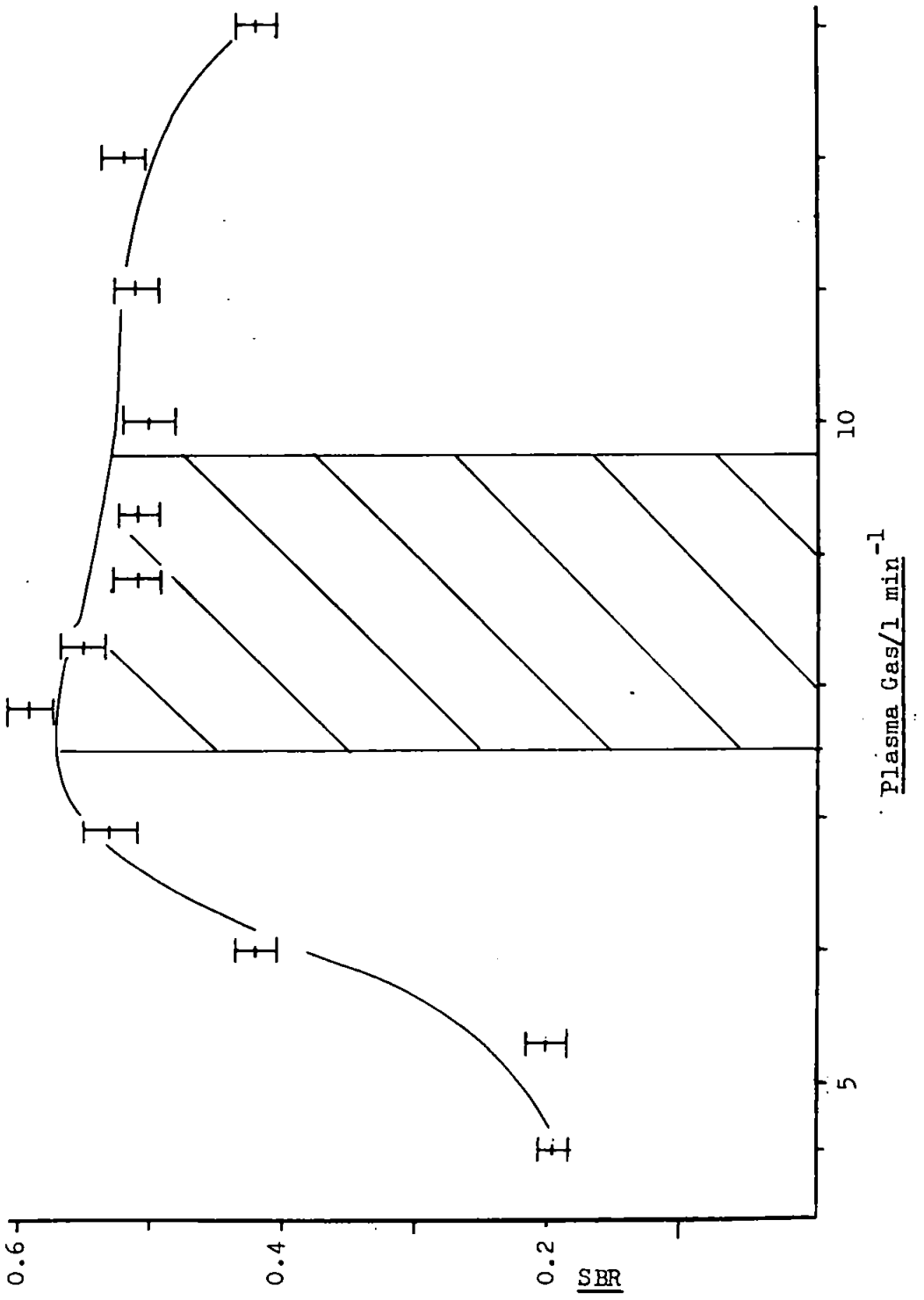


Figure 31(c)

Univariate Search for Argon Purge Gas Flow Rate

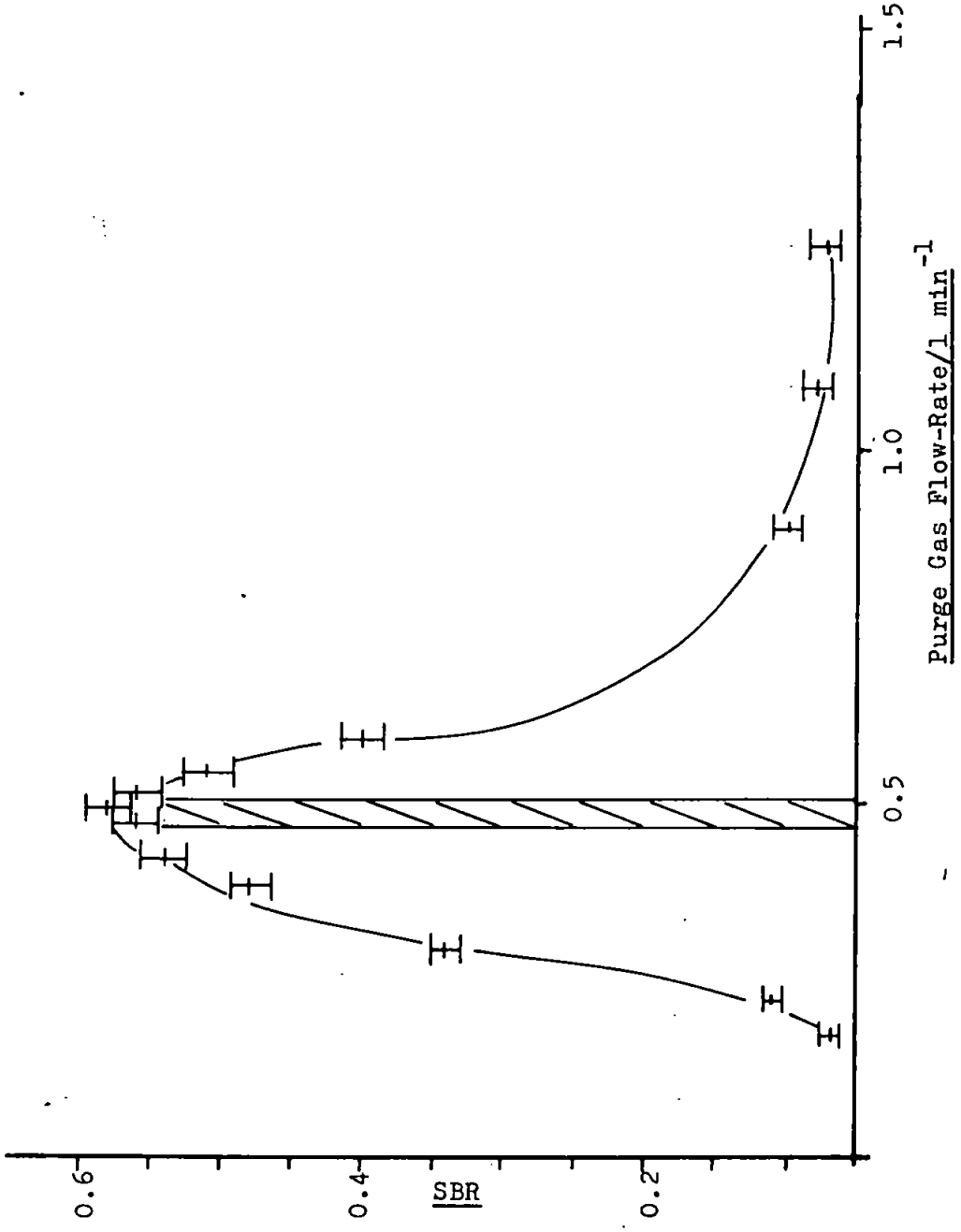


Figure 31(d)

Univariate Search for Viewing Height

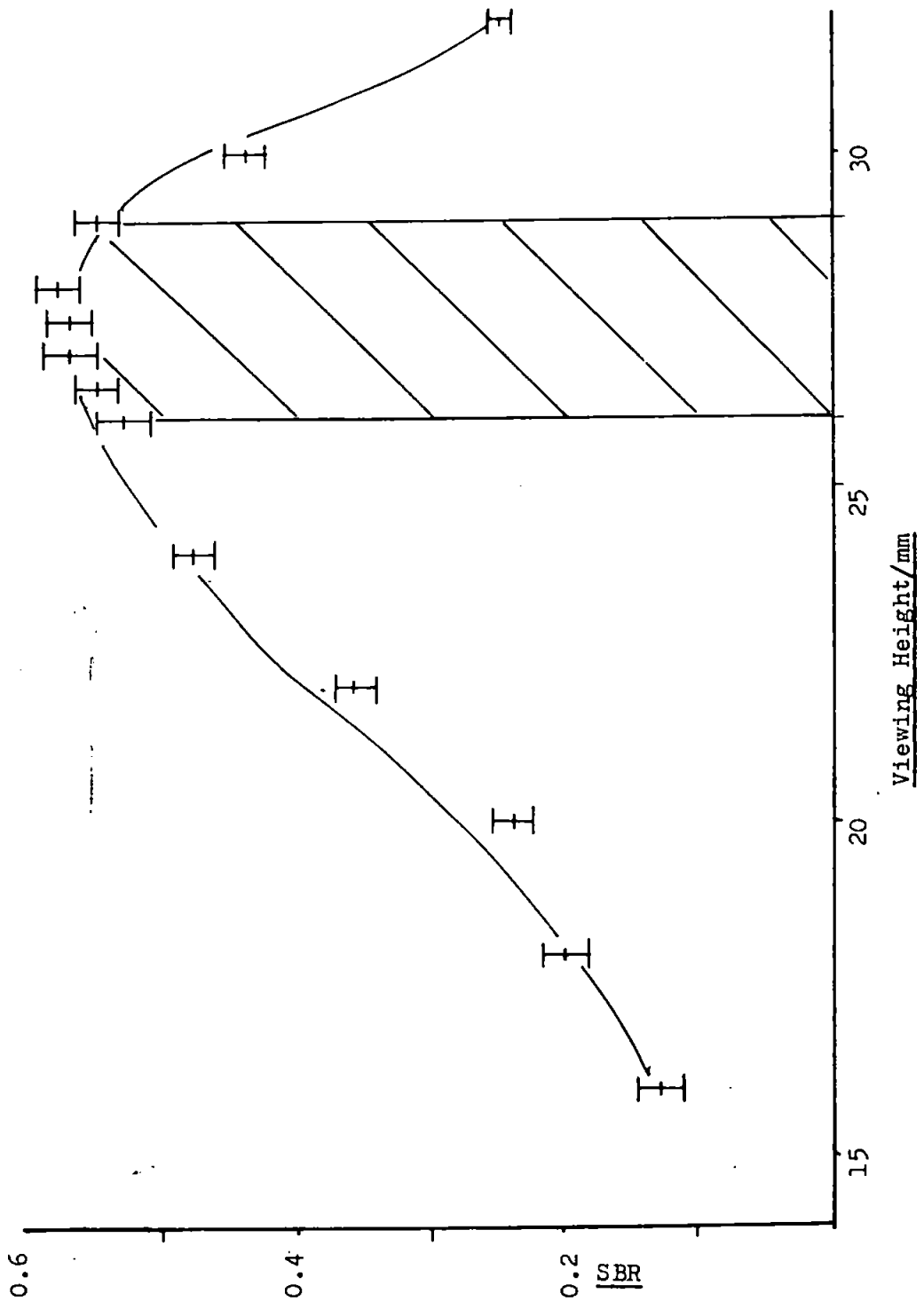
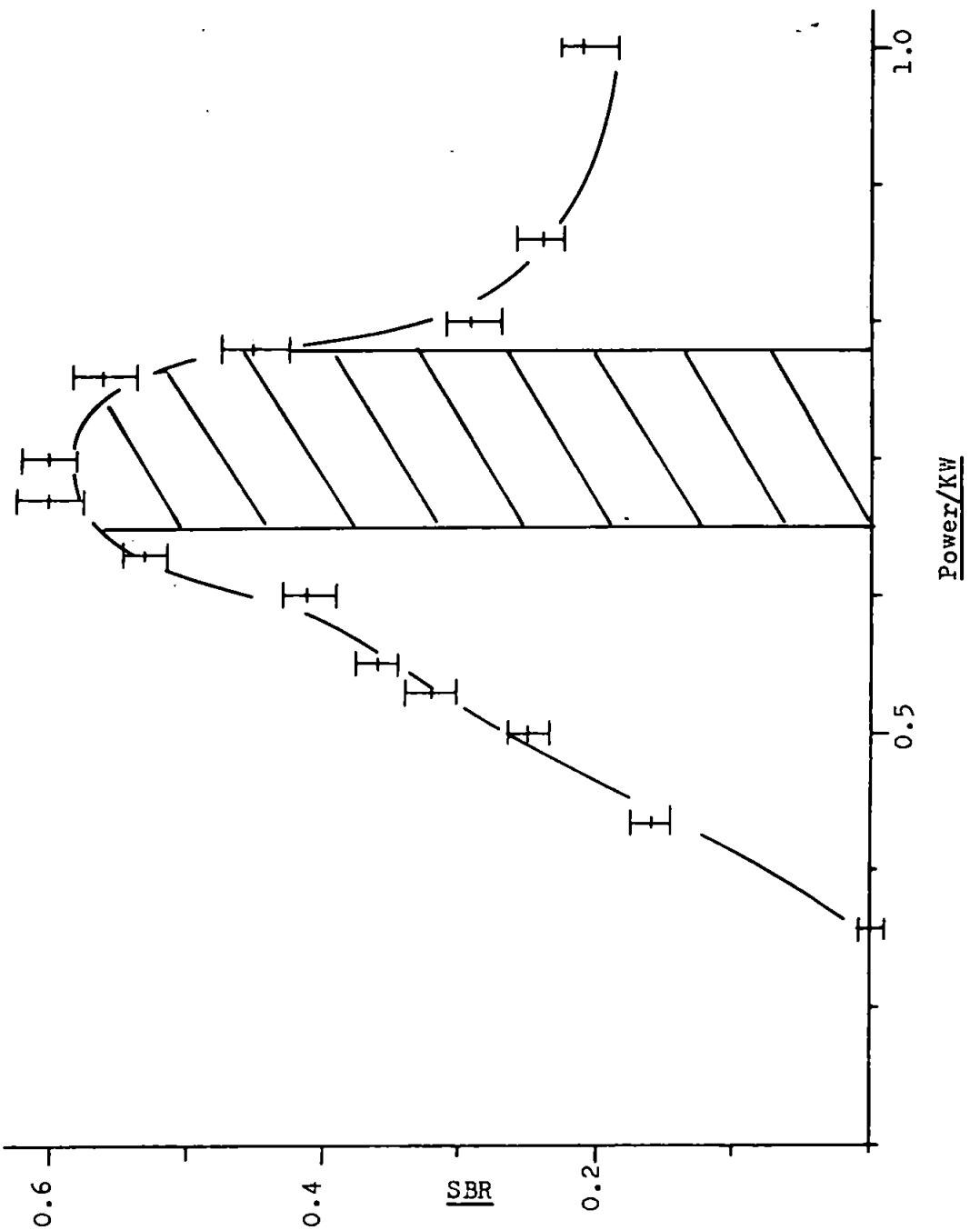


Figure 31(e)

Univariate Search for Power Coupled into the Plasma



the shaded area indicating the range of values in the final simplex set. These searches indicate the success of the optimisation and show the purge gas, Fig. 31(c), to be a very critical parameter. At low purge gas flows, 150 ml min^{-1}, there is insufficient velocity to punch a path through the plasma fireball, resulting in a low SBR. At high purge gas flows, 1 l min^{-1}, the residence time of the analyte in the plasma is reduced, again yielding a low SBR. Similar sensitivity to injector gas flow-rate has been reported for solution work by Ebdon et al. (314). The SBR is relatively insensitive to change in plasma gas flow-rate, Fig. 31(b), whereas for the coolant flow-rate, Fig. 31(a), the background emission remains relatively constant but above 7 l min^{-1} the arsenic emission decreases rapidly, thus decreasing the SBR. This is probably related to the increased size of the plasma at these high coolant flow-rates which thus caused a reduction in the power density within the plasma. For the viewing height, Fig. 31(d), as the height of observation approaches the load coils, the arsenic emission increases up to within 20 mm. of the load coil when it starts to decrease. The background emission increases as one approaches the load coils and also when the viewing height is further than 30 mm. from the coil. The latter increase is probably due to molecular emissions in the cooler tail flame whereas the former increase in background probably results from continuum emission from the plasma fireball.

To test the effect of hydrogen on the SBR, an arsenic solution (100 mg l^{-1}) was nebulized into the plasma using a Babbington type nebulizer (315) under both the solution optimum and hydride optimum conditions. The experiment was carried out with and without the addition of hydrogen, 72 ml min^{-1}, to the injector gas and the results may be seen in Table 32.

Table 32

Effect of Hydrogen on Signal to Background Ratio

	Hydride Optimum Conditions			Solution Optimum Conditions		
	Signal (mV)	Background (mV)	SBR	Signal (mV)	Background (mV)	SBR
Without H_2	13	104	0.125	280	480	0.58
With H_2	70	670	0.13	230	955	0.24

Under the solution optimum conditions, the addition of hydrogen to the injector flow causes a marked increase in background emission coupled with a slight decrease in signal, thus giving an overall large decrease in SBR. Under the hydride conditions addition of hydrogen again causes an increase in background emission; however, in this case a similar increase in signal intensity occurs with the result that the SBR is virtually unchanged. Thus the optimisation moved the plasma conditions to a region of factor space where the increase in background emission caused by the addition of hydrogen is cancelled out by an increased response to arsenic. The success of the simplex may be seen in more tangible ways from the detection limits obtained for the four arsenic species, Table 30, column 3. Although both FAAS and FAFS give better detection limits, ICP-OES has the advantage that the linear range obtained is much greater and that multi-element work is possible.

7.7.4 Speciation of Arsenic Compounds using Inductively Coupled Plasma Optical Emission Spectroscopic Detection

The chromatographic and hydride generation conditions were the same as for the previous couplings, see section 7.5. The gas which purged the arsines from the gas/liquid separator also transported the arsines up to into the plasma.

The separation of the four arsenic species obtained was, as would be expected, very similar to those achieved using FAAS and FAFS detection, Fig. 27. The detection limits and linear ranges were evaluated for the arsenic species, Table 30. The detection limits were poorer using ICP-OES but the linear range, Table 33, was greater. The linearity was not evaluated above 20 ppm for arsenite, or above 40 ppm for the three other arsenic species, since such levels were unlikely to be encountered in the environment. The main advantage of ICP-OES over the other detection methods used is that it offers the possibility of multi-element detection.

Table 33

Linear Ranges for Arsenite/mg l^{-1}

ICP-OES	0.5 - 20
AAS	0.2 - 6.0
AFS	0.1 - 5.0

7.8 CONCLUSION

The detection limits obtained for the four arsenic species using the three modes of detection, Table 30, show FAFS to be the most sensitive. The detection limits obtained using FAAS are only slightly worse than FAFS and as a technique for routine use FAAS is far more reliable and less source dependant. Comparison of the linear ranges obtained using the different spectroscopic techniques, Table 33, shows up the limitation of absorption techniques, namely, short linear ranges. The linear range for FAFS is disappointingly narrow; however, this is probably related to the inability to operate the light source at sufficient intensity since one would expect the linear range of a fluorescence technique to extend below that obtained for FAAS rather than to higher concentrations. The linear range using the ICP was not tested above 20 mg l^{-1} since it was felt that environmental samples containing such levels of arsenic would be rare. Comparison of the detection limits obtained for arsenite using the HPLC system and standard continuous flow hydride generation (304) for total arsenic, Table 34, shows that the use of HPLC causes a deterioration in detection limits. This

Table 34

Comparison of Detection Limits for Arsenite

	D.L./ng cm^{-3}		
	AAS	AFS	ICP
Total	0.8[a]	0.34[a]	14
HPLC	9.4	6.1	51

(a) From reference 304

illustrates the increase in imprecision caused by the injection and also by the measurement of a transient signal, however, this deterioration in the detection limits is more than compensated for in the increased information about speciation which the coupled systems yield.

The coupled HPLC-atomic spectroscopy systems developed compare favourably with both graphite furnace couplings (218, 231-233, 237, 239) and the ion chromatography system of Ricci et al. (237). The couplings developed allow speciation of the four species in under ten minutes which is superior to any of the other coupled techniques for arsenic speciation.

The disadvantage of hydride generation is that it is only applicable to reducible species, and thus would be of little use for the determination of non-reducible species, such as arsenobetaine or arsenocholine.

8 FUTURE WORK AND CONCLUSIONS

8.1 FUTURE WORK

8.1.1 Gas Chromatography - Atomic Spectroscopy

The ready applicability of the developed GC-FAAS couplings to the speciation of various metallic moieties has been demonstrated in Chapter 6. Two other possible areas of interest arise from the relative volatilities of TML and TEL. If the headspace above a solution is sampled, 1 cm^3, and injected into the GC-FAAS system, Fig. 32, then a response is obtained for TML only. Thus if an organometallic species is sufficiently volatile it may be determined without recourse to extensive sample manipulation, which may affect the speciation of the metal in the original sample. For example, in the study of the possible methylation of lead compounds to TML, the rate of methylation could be followed by headspace sampling.

The relative involatility of TEL suggests possible forensic and industrial health applications. It proved possible to demonstrate that skin has been in contact with petrol up to seven hours after the event. This was achieved by swabbing the skin and analysing the extract by GC-FAAS. The presence of TEL gave an unequivocal marker of petrol contact. The use of electron capture or flame ionization yields ambiguous data since swabbing of the skin also extracts many other organic compounds, making chromatographic data difficult to interpret. The presence of TML was not found if the swabbing occurred any later than fifteen minutes after the initial contact with the petrol.

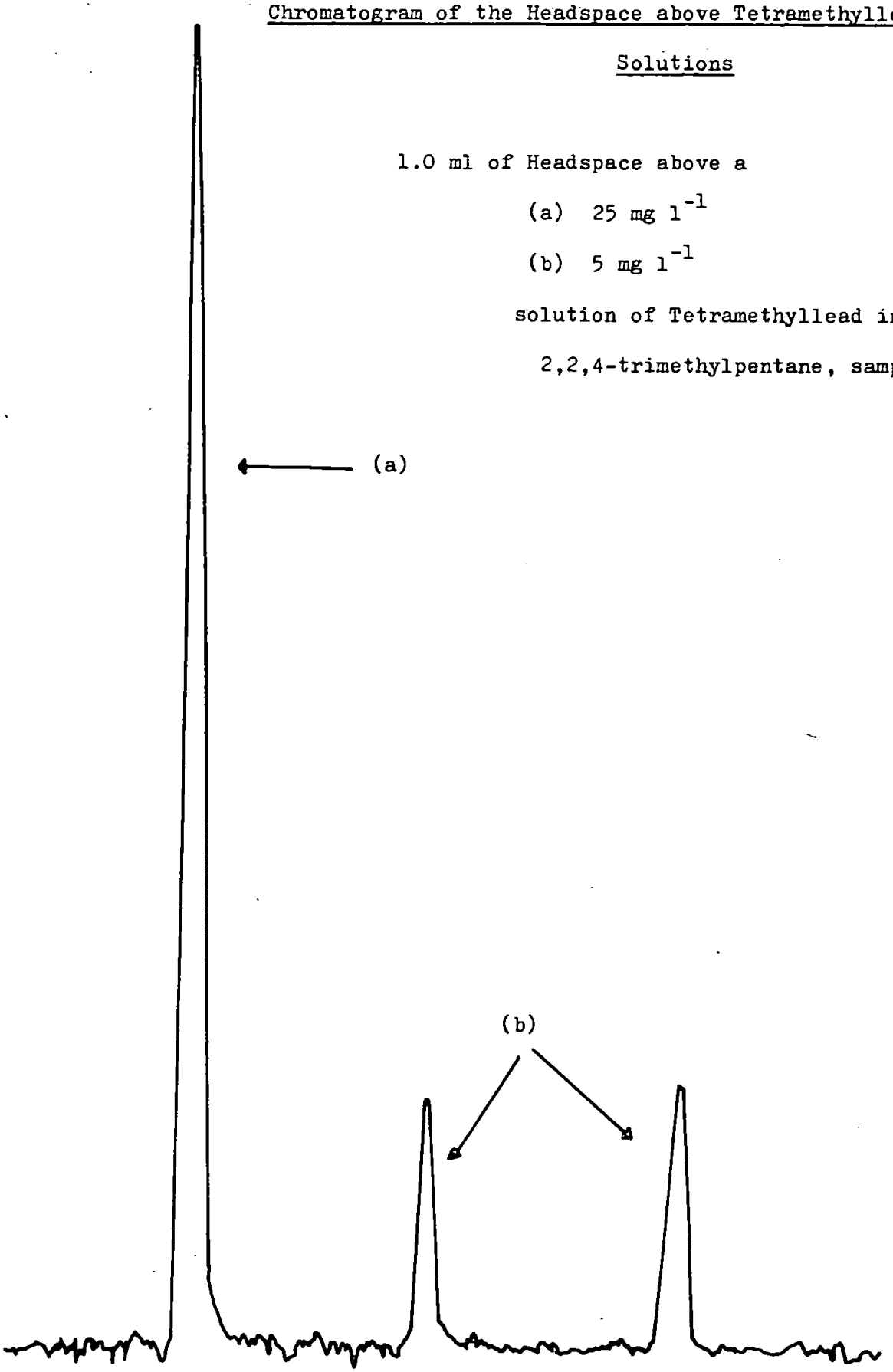
Figure 32 Gas Chromatography - Flame Atomic Absorption Spectroscopy Chromatogram of the Headspace above Tetramethyllead Solutions

1.0 ml of Headspace above a

(a) 25 mg l^{-1}

(b) 5 mg l^{-1}

solution of Tetramethyllead in 2,2,4-trimethylpentane, sampled.



The fate of organometallic compounds in the environment is a field in which the specificity of the information obtained using coupled GC-FAAS would be valuable. The behaviour of TML and TEL in both distilled and sea water was given some preliminary consideration. A solution of TML and TEL in acetone was added to the water and the sample continually agitated, so as to mimic a flowing water course. The water was sampled periodically, the tetraalkyllead compounds extracted with hexane and determined by GC-FAAS. Initial experiments in the open laboratory indicated that the rate of degradation was related to the amount and intensity of sunlight entering the laboratory. Thus, follow-up experiments under ultraviolet, UV, light and also in the dark were performed. The results of these experiments are shown in Figures 33-35. There was minimal degradation of either TML or TEL, Fig. 33, over a four-hour period in distilled water under UV radiation, whereas in sea water, Fig. 34, under the same conditions a rapid degradation was observed for both TML and TEL over a similar time period. Under conditions of total darkness degradation of the tetralkyllead compounds still occurred, Fig. 35, but at a much slower rate, the time span of the experiment being fifty hours. Obviously much more work is required in this field; however, from the above it can be inferred that the degradation follows a free radical mechanism which is catalysed by UV light and in which chloride ions from the sea water play an important role.

8.1.2 Liquid Chromatography

There exists, both within this Institution and elsewhere, a considerable interest in arsenic transformations in the environment. In the Devon area, interest is stimulated by the gross arsenic pollution which

Figure 33 Degradation of Tetraalkyllead Compounds in Distilled Water Under Ultraviolet Light (365 nm)

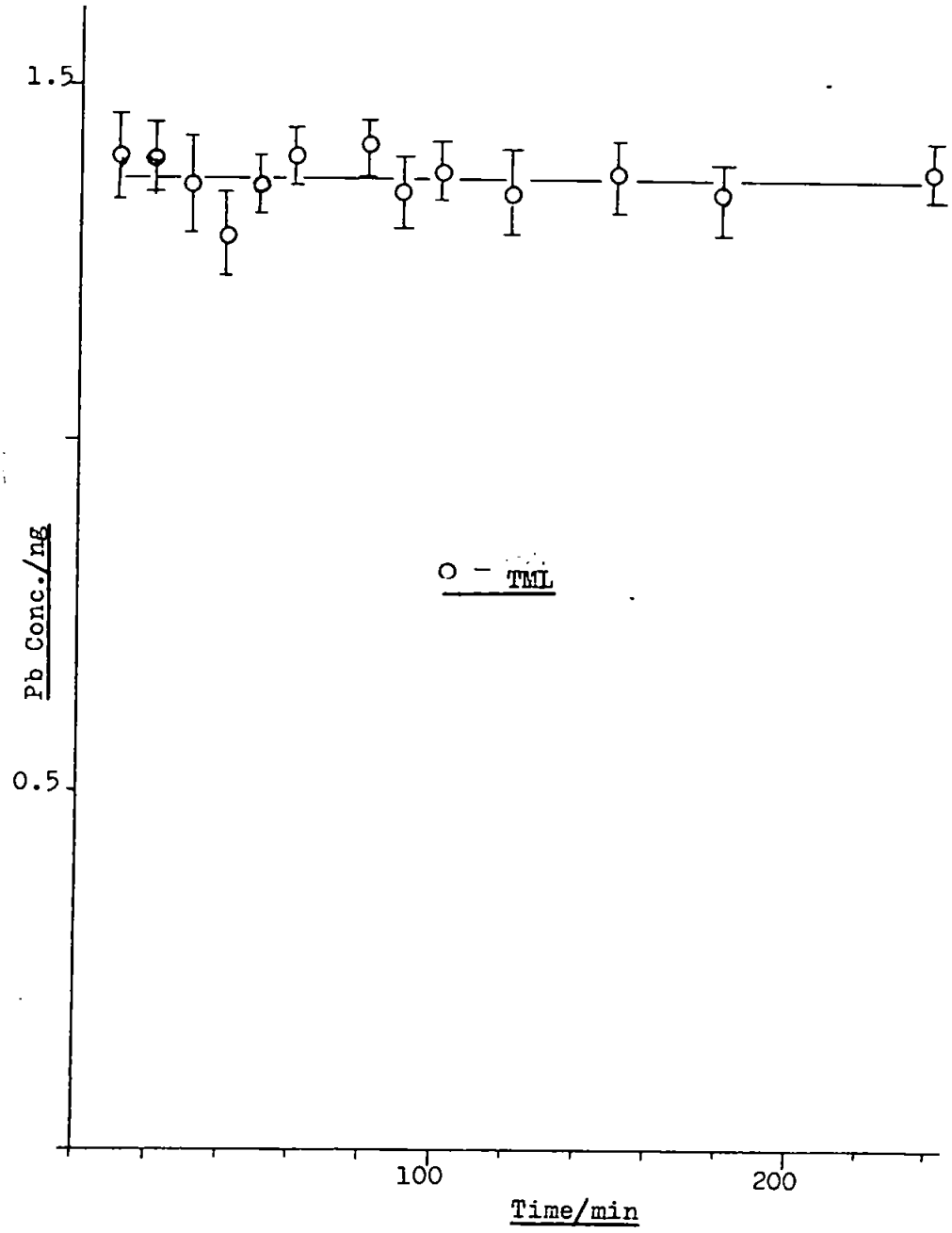


Figure 34 Degradation of Tetraalkyllead Compounds in Sea Water Under Ultraviolet Light (365 nm)

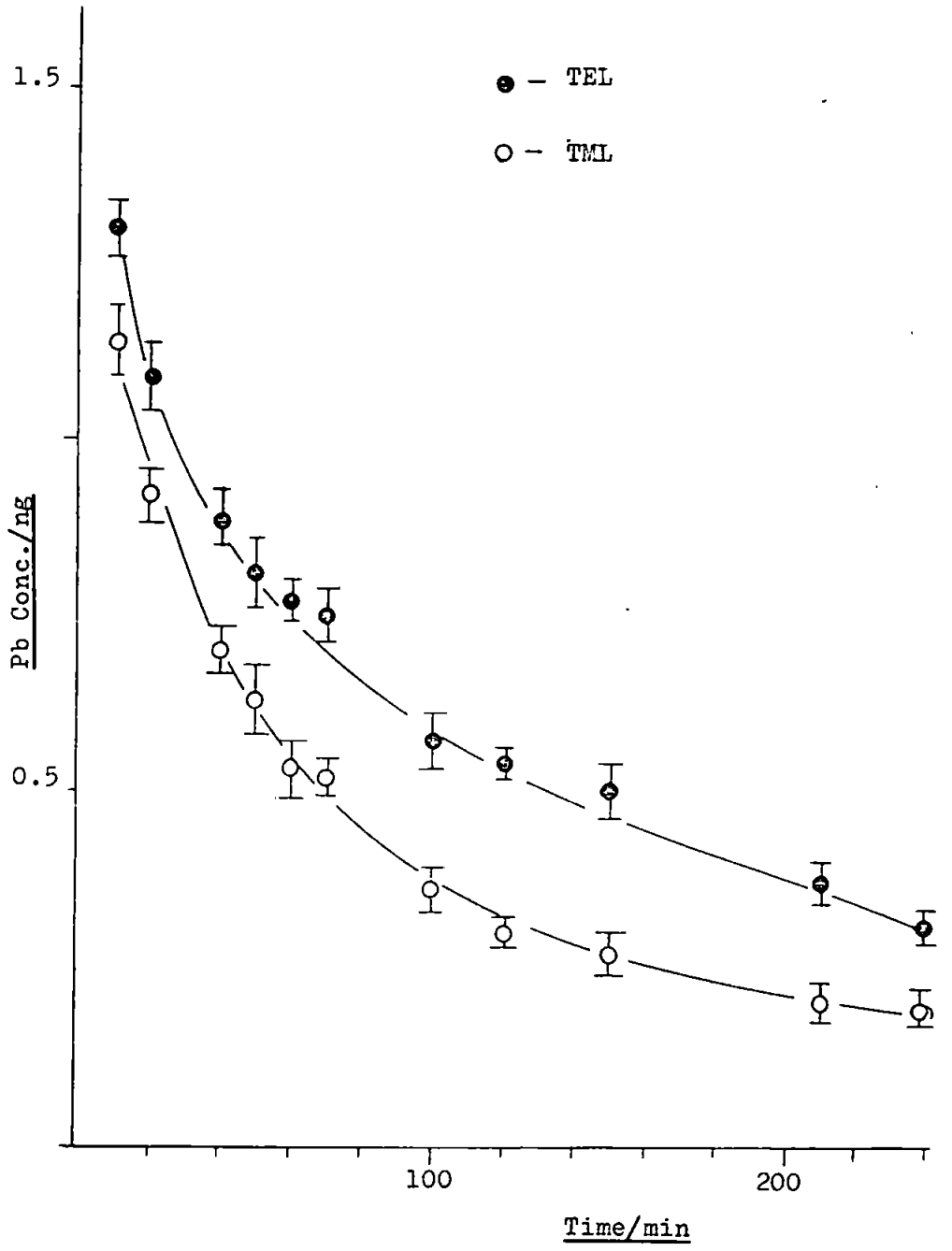
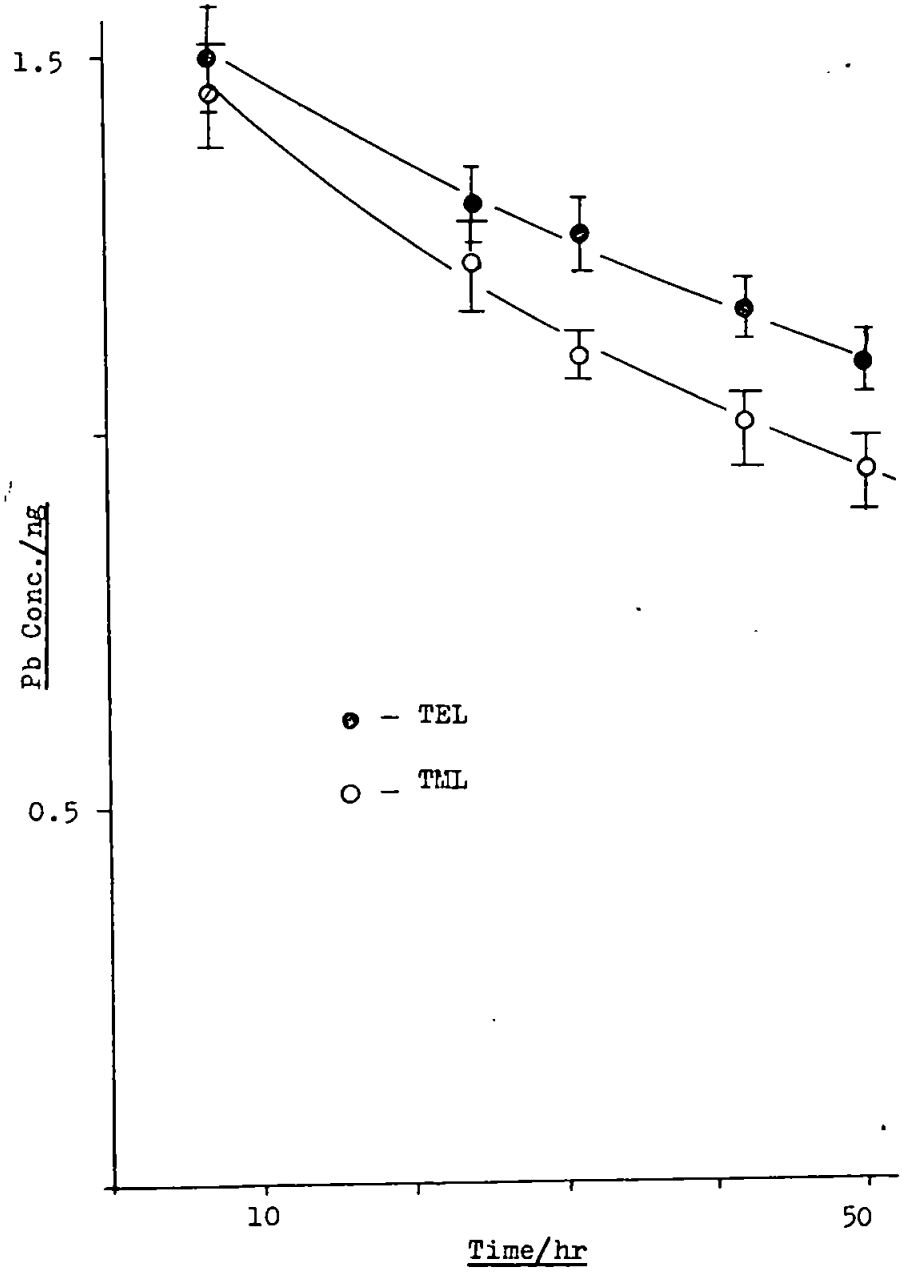


Figure 35 Degradation of Tetraalkyllead Compounds in Sea Water

In Total Darkness



is a legacy of previous smelting of arsenous ores. The occurrence and fate in both pore and sea water environments could be monitored using the HPLC-hydride-FAAS coupling developed, Chapter 7. The sensitivity of the separation towards ionic strength, however, would entail either prior extraction of the arsenic from sea water or design of a new chromatographic process. The former is to be avoided if possible, since it may affect the arsenic speciation, thus leading to false conclusions as to the species in the original sample. Changing the chromatography would appear to be the better option. Ion pair chromatography may prove to be the way forward for the separation of arsenic species in pore water samples, and is readily interfaced with the hydride-FAAS system developed.

8.2 CONCLUSIONS

The work presented has demonstrated the advantages of metal specific detection for trace metal speciation studies, these being unequivocal chromatographic interpretation and the ability to withstand less than optimal chromatographic resolution. The traditional disadvantage of FAAS of poor detectability has, by careful consideration of atom cell design/optimisation and with due attention to atomic residence times, been overcome. The drawback of short linear working ranges found with absorption techniques remains for each atom cell designed; however, with the GC-FAAS coupling removal of the ceramic tube enables a linear range of 0.1-300 ng to be utilized. The atom cells developed for GC-FAAS have the added attraction that simplicity, robustness, low cost and ready demountability has been coupled with excellent detectability for volatile organometallic species.

The coupling of liquid chromatography with atomic spectroscopy *via* hydride generation illustrated again that FAAS can provide highly sensitive metal detection. The coupling with ICP-OES demonstrated the advantage of using an emission technique, in that longer linear working ranges are easily obtained. The limitations of low nebulization efficiency encountered when introducing liquids to flames or plasmas were circumvented in this case by generating a volatile derivative prior to introduction to the atom cell. Unfortunately this approach is limited hence nebulization efficiencies must either be improved or avoided by other means if adequate detection levels are to be achieved.

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Glossary for Tables 1 to 9

acac	Acetylacetonate
AW	Acid washed
BAA	Benzoylacetylacetonate
bn	Butylenediamine
CDTA	1,2 - cyclohexylenedinitrilotetracetic acid
DEDML	Diethyldimethyllead
DEDTC/dtc	Diethyldithiocarbamate
DMA	Dimethylarsonic acid
EGTA	Ethylenebis (oxyethylenenitrilo) tetraacetic acid
en	Ethylenediamine
$enAA_2$	N, N^1 - ethylenebis (acetylacetoneimine)
$enTFA_2$	N, N^1 - ethylenebis(trifluoroacetylacetoneimine)
ETML	Ethyltrimethyllead
$H_2(enSal_2)$	N, N^1 - ethylenebis (salicyladiamine)
HFA/hfa	Hexafluoroacetylacetonate
MMA	Monomethylarsonic acid
MMT	Methylcyclopentadienylmanganesetricarbonyl
MTEL	Methyltriethyllead
ODS	Octadecasilane
OMP 2	Poly (tri-n-butyltinmethacrylate-tri-n-propyltin-methacrylate-methylmethacrylate)
OMP 2	Poly (tri-n-butylmethacrylate-methylmathacrylate)
OMP 4	Tri-n-butyltin ester of poly (methylvinylether-maleic anhydride)
OSM	Oscillating slit mechanism
PAM	2,2 - dimethylhexane - 3,5 - dionato ligand

p-APA	p-Aminophenylarsonate
PBB	Polybrominated biphenyls
PD	5 - nitro-o-phenylenediamine
pn	Propylenediamine
RPC	Reverse phase chromatography
SEC	Size exclusion chromatography
TBA	Tributylammonium ion
TBAP	Tributylammonium phosphate
TBP	Tributylphosphate
T_c	Chromatographic Temperature
TEL	Tetraethyllead
TES	2 {[2 - hydroxy-1,1-bis (hydroxymethyl) ethyl] amino} ethanesulphonate
TFA/tfa	Trifluoroacetylacetone
THAN	Tetraheptylammonium nitrate
THF	Tetrahydrofuran
T_I	Injector Temperature
T_{in}	Interface Temperature
TMCS	Trimethylchlorosilane
TMFS	Trimethylfluorosilane
TML	Tetramethyllead
TMS	Tetramethylsilyl-
TMT	Tetramethyltin

Lectures and Meetings Attended

(i) Selected lectures from the C.N.A.A. M.Sc. in Instrumental Chemical Analysis (Sheffield City Polytechnic)

(ii) Department of Chemistry 'Analytical Discussion Group', Sheffield City Polytechnic, weekly from October, 1979 to December, 1980.

(iii) Department of Chemistry Research Colloquia, Sheffield City Polytechnic, fortnightly from October, 1979 to December, 1980.

(iv) Modern Methods of Analysis Group of the Sheffield Metallurgical and Engineering Association, fortnightly meetings from October, 1979 to December 1980.

(v) Chemistry of Natural and Polluted Environments Research Group, Plymouth Polytechnic, weekly from January, 1981 to November, 1982

Meetings of Royal Society of Chemistry

(i) Atomic Spectroscopy Group, joint meeting with North East Region R.I.C., 'Competitive Spectroscopies in Metallurgical Analysis', Sheffield, December 5th, 1979.

(ii) Atomic Spectroscopy Group, joint meeting with the Board of Annual Reports on Analytical Atomic Spectroscopy, 'Seventh Annual Reports on Analytical Atomic Spectroscopy Symposium', Sheffield, March 27th, 1980.

(iii) Analytical Division 'Research and Development Topics in Analytical Chemistry', Canterbury, April 1st/2nd, 1980.

(iv) Atomic Spectroscopy Group with North West Region R.S.C., 'Industrial Applications of Atomic Absorption Spectroscopy', Lancaster, September 16th, 1980.

(v) R.S.C. Autumn Meeting: Analytical Division Symposium on 'Trace and Ultra-Trace Analysis', Cardiff, September 23rd-25th, 1980.

(vi) Industrial Division, joint meeting with North East Region R.S.C., 'Industrial Hygiene Monitoring', Sheffield, December 3rd, 1980.

(vii) Atomic Spectroscopy Group, joint meeting with North East Region R.S.C., 'Plasma Emission Spectroscopy', Middlesborough, March 11th, 1981.

(viii) Atomic Spectroscopy Group, joint meeting with the Board of Annual Reports on Analytical Atomic Spectroscopy, 'Eighth Annual Reports on Analytical Atomic Spectroscopy Symposium: 'Quality Assurance and Atomic Spectroscopy', Sheffield, April 2nd, 1981.

(ix) Royal Society of Chemistry Annual Chemical Congress: Analytical Division Symposium: 'Matrix and Sensitivity Problems in Analysis', Guildford, April 7th-9th, 1981.

(x) Analytical Division 'Research and Development Topics in Analytical Chemistry', Salford, June 30th/July 1st, 1981

(xi) Atomic Spectroscopy Group, joint meeting with the Board of Annual Reports on Analytical Atomic Spectroscopy, the Institute of Physics and the Modern Methods of Analysis Group of the Sheffield Metallurgical and Engineering Association. The Ninth Annual Reports on Analytical Atomic Spectroscopy Symposium: 'Developments in Trace Metal Determinations', Sheffield, April 1st, 1982.

(xii) Analytical Division, 'Research and Development Topics in Analytical Chemistry', Hull, 6th/7th July, 1982.

(xiii) Atomic Spectroscopy Group, joint meeting with the Institute of Physics Spectroscopy Group, 'The First National Atomic Spectroscopy Symposium', Sheffield, 13th-15th July, 1982.

(xiv) Royal Society of Chemistry Autumn Meeting, Analytical Division Symposium: 'Spectrochemical Detectors in Chromatography', Edinburgh, 21st-23rd September, 1982.

(xv) Atomic Spectroscopy Group, current awareness symposium on 'Electrothermal Atomization in Analytical Atomic Spectroscopy', Bristol, 4th November, 1982.

Publications

(i) "Approaches to Trace Metal Speciation in Environmental Samples"
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(ii) "Development and Optimisation of Atom Cells for Sensitive Coupled Gas Chromatography - Flame Atomic Absorption Spectroscopy"
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